**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY**

# INVESTIGATION OF PHYSICAL AND MECHANICAL PROPERTIES OF POLYURETHANE NANOCOMPOSITES PREPARED USING DIFFERENT TYPES OF NANO ADDITIVES

**M.Sc. THESIS**

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**Department of Polymer Science and Technology**

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**MAY 2014**

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**Thesis Advisor: Prof. Dr. Nurseli UYANIK**

**MAY 2014**

**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

# FARKLI NANO KATKILAR İLE HAZIRLANAN POLİÜRETAN NANOKOMPOZİTLERİNİN FİZİKSEL VE MEKANİK ÖZELLİKLERİNİN İNCELENMESİ

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**Tez Danışmanı: Prof. Dr. Nurseli UYANIK**

**MAYIS 2014**

**Bahar BÜYÜKKAHRAMAN**, a M.Sc Student of ITU **Institute of Science and Technology/Graduate School of Istanbul Technical University student** ID 515101030, succesfully defended the **thesis** entitled **"Investigation of Physical and Mechanical Properties of Polyurethane Nanocomposites Prepared Using Different Types of Nano Additives"**, which she prepared after fulfiling the requirements specified in the associated legislations, before the jury whose signatures are below.

| | | |
|---|---|---|
| **Thesis Advisor :** | **Prof. Dr. Nurseli UYANIK**<br>Istanbul Technical University | ..... |
| **Jury Members :** | **Assoc. Prof. Dr. Orhan GÜNEY**<br>Istanbul Technical University | ..... |
| | **Prof. Dr. Ayfer SARAÇ**<br>Yıldız Technical University | ..... |

**Date of Submission : 5 May 2014**
**Date of Defense : 29 May 2014**

***To my mother,***

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May 2014

Bahar BÜYÜKKAHRAMAN
Chemical Engineer

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**ABBREVIATIONS**

| | |
|---|---|
| **PU** | **:** Polyurethane |
| **NCO** | **:** Isocyanate |
| **MDI** | **:** Methylene diphenyl diisocyanate |
| **TDI** | **:** Toluene diisocyanate |
| **XDI** | **:** Xylene diisocyanate |
| **HXDI** | **:** Hydrogenated xylene diisocyanate |
| **DBDI** | **:** 4,4'-dibenzyl diisocyanate |
| **IPDI** | **:** Isophorone diisocyanate |
| **HDI** | **:** Hexamethylene diisocyanate |
| **HDA** | **:** Hexamethylene diamine |
| **IPDA** | **:** Isophorone diamine |
| **MDA** | **:** Methylene dianiline |
| **MW** | **:** Molecular weight |
| **MWD** | **:** Molecular weight distribution |
| **PET** | **:** Polyethylene terephthalate |
| **DBTDA** | **:** Dibutyltin diacetate |
| **DBTDL** | **:** Dibutyltin dilaurate |
| **DIDP** | **:** Diundecyl phthalate |
| **DOP** | **:** Dioctyl phthalate |
| **HR** | **:** High-resilience |
| **EA** | **:** Energy-absorbing |
| **TPU** | **:** Thermoplastic polyurethane |
| **PCNs** | **:** Polymer/clay nanocomposites |
| **PLS** | **:** Polymer layered silicate |
| **MMT** | **:** Montmorillonite |
| **HNT** | **:** Halloysite nanotube |
| **FTIR** | **:** Fourier transform infrared spectroscopy |
| **TGA** | **:** Thermal Gravimetric Analysis |
| **XRD** | **:** X-ray diffraction |
| **MMT** | **:** Montmorillonite |
| **HNT** | **:** Halloysite nanotube |

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# INVESTIGATION OF PHYSICAL AND MECHANICAL PROPERTIES OF POLYURETHANE NANOCOMPOSITES PREPARED USING DIFFERENT TYPES OF NANO ADDITIVES

## SUMMARY

Polyurethane (PU), which is found by Otto Bayer and his colleagues in 1937, is formed from organic unit chains that containing urathane linkages. “Polyurethane” contains the reaction product between isocyanate and hydroxyl group in the form of repeat unit. The morphology of the polymer is preformed according to used diol and isocyanate’s character and molecular structure. Polyurethanes have different usage areas due to their structures, they can ve thermosets or thermoplastics. While the flexible polyurethane foams are used in furniture sector, rigid polyurethane foams are used in wall and roof insulation. Thermoplastic polyurethanes can be used in many fields, such as medical devices, sporting goods, adhesives, fillers and automotive industry etc.

The basis of nanotechnology is studying molecular size and obtain large structures from the renovated molecular structures. The properties of materials of nanometric size differ from the same material properties in macro size. Nanocomposites, nanometer-sized particles in a matrix formed by the dispersion of the materials. Nanoscale materials, which are for generating improved properties nanocomposites, are used with the ceramic, metal or polymer material as a promoter additive. Advantages of the widely used nanocomposites may be listed as increasing the modulus, material strengthening, prevent leakage of gas to the material, reduction of flammability. One of the major advantages of nanocrystalline inorganic additives is increasing the thermal stability of nanocomposites. In many applications, it is desirable that the heat stable polymeric material.

Different methods are applied in order to increase the thermal conductivity of polymers in academic researches and in industry. One of them is adding the high thermal conductivity granules or fibers to the polymer during the production. Addition of these types of particles increases the thermal conductivity of the polymer. One of the widely used reinforcement material for polymeric nanocomposite material is clay. Clays are preferred because of its layered structure, being inexpensive and found possibility in nature abundantly. The layer structured clay minerals are very good additive material due to the ability of dispersion in polymer solutions.

The aim of this study was the investigation of physical and chemical behaviours of nanosized halloysite, sepiolite and bentonite in polyurethane nanocomposite structure; which were added in prepolymeric form of polyurethane. The based of this study is adding the different percentages of nano additive into the polyurethane prepolymer and then providing the curing in the presence of catalyst. In this way, 15 samples were prepared and the results have been observed as thermally, chemically

and mechanically. FTIR, TGA, XRD and mechanical analysises were utilized for the characterization of the samples.

Firstly, nano additive were waited in the toluene solvent for 1 hour to ensure its swelling. Secondly, prepared solvent-nano additive mixture were added to polyurethane prepolymer and all mixture were heated at 80ºC. Then, catalyst was added the PU/ nano additive/solvent mixture and stirred 2 minutes with magnetic stirrer. Mixed solution was poured to straight mouled and placed in the vacuum oven at 80ºC. Samples were waited in the vacuum oven. After 4 hour, samples were taken from oven and settled to the desiccator for 1 hour. Finally, cured samples were used for testing.

Samples are analysed by FTIR spectrophometer between 500 and 4000 $cm^{-1}$. Polyurethane sample cured alone, has all characteristic polyurethane peaks. It was observed that specific polyurethane spectrums of polyurethane samples cured by halloysite, sepiolite, activated and raw bentonite nano additives, were shown.

Aim of the XRD analysis is observing the degree of "layer spacing" during the curing of the nano additive in the polyurethane nanocomposites (PUNC). Analysis results showed that nano additive layers were distributed in the sepiolite/ polyurethane nanocomposite structure.

TGA analysis of Clay/PUNC samples were carried out between 0-800 ºC. According to TGA analysis of clay/PUNC samples, it is found out that clay minerals had positive effect on the decomposition temperature of a polymeric polyurethane nanocomposites. Increased amount of halloysite, sepiolite, raw bentonite and activated bentonite also increased the decomposition temperature of polymeric polyurethane, and each nano clay structure also showed different thermal behavior compared to each other. Examining a certain (7.0%) amount of halloysite, sepiolite, raw and activated bentonite into the polymeric polyurethane showed that; halloysite shifted the pure polyurethane polymer decomposition temperature from 450ºC to 515ºC, sepiolite shifted this temperature to 525ºC, raw bentonite shifted temperature to 495ºC,and finally activated bentonite shifted the temperature to 500ºC. According to the results of our study; sepiolite and halloysite have better thermal performance than raw bentonite and activated bentonite as an additive in polyurethane.

According to the results of mechanical tests, increased amount of halloysite within the polymeric polyurethane structure increased tensile strength, elongation at break and elastic modulus values. Addition of sepiolite into composite structures increased the tensile strength and elongation at break values to some extent but further addition showed a bell shaped behaviour. In addition, sepiolite did not affect the elastic modulus of the polymeric structure. Addition of raw bentonite increased the elastic modulus and tensile strength of polymeric polyurethane but it did not affect the amount of elongation at break. Activated bentonite addition increased the elongation at break and tensile strength of polymeric polyurethane but it did not affect the amount of elastic modulus.

# FARKLI NANO KATKILAR İLE HAZIRLANAN POLİÜRETAN NANOKOMPOZİTLERİNİN FİZİKSEL VE MEKANİK ÖZELLİKLERİNİN İNCELENMESİ

## ÖZET

Poliüretan (PU), 1937 yılında Otto Bayer ve çalışma arkadaşları tarafından bulunan, karbamat bağlantıları içeren organik üniteler zincirinden oluşan polimerlerdir. İzosiyonat ve hidroksil grupları arasındaki reaksiyon ürünü olan polimer "poliüretan" olarak adlandırılır. Polimerin morfolojisi; kullanılan diol ve izosiyanatın molekül yapısı ve karakterine göre değişir. Poliüretanlar yapılarına göre değişik kullanım alanlarına sahiplerdir. Termoset ve termoplastik olabilirler. Esnek poliüretan köpükler mobilya sektöründe kullanılırken, sert poliüretan köpükler duvar ve çatı yalıtımlarında kullanılmaktadır. Diğer bir poliüretan çeşidi olan termoplastik poliüretanlar; tıbbi cihazlar, spor ürünleri, yapıştırıcılar, dolgu malzemeleri ve otomotiv sektörü gibi çok çeşitli alanlarda kullanım imkanı bulmaktadır.

Nanoteknolojinin temeli, moleküler boyutta çalışarak, moleküler yapısı yenilenmiş büyük yapılar elde etmektir. Malzemelerin nanometrik boyuttaki özellikleri, aynı malzemenin makro boyuttaki özelliklerine göre değişiklik göstermektedir. Nano kompozitler, bir matris içerisinde nanometre büyüklüğünde parçacıkların dağılması ile oluşan malzemelerdir. Nanoboyuttaki malzemeler, gelişmiş özelliklere sahip nanokompozitleri oluşturmak üzere seramik, metal ya da polimer gibi malzemeler içinde destekleyici katkı maddesi olarak kullanılmaktadır. Günümüzde kullanım alanı oldukça yaygınlaşan nano kompozitlerin, malzemeye getirdiği üstünlükler; modülü arttırması, güçlendirmesi, malzemenin gaz geçirgenliğini engellemesi, yanıcılığını azaltması olarak sıralanabilir. Nanokompozitlerin önemli avantajlarından biri de nanoboyutlu inorganik katkı maddelerin ısıl kararlılığını arttırmasıdır. Birçok uygulamada, polimerik malzemenin farklı sıcaklıklarda ve uzun zamanlı kullanımda önemli oranda boyutunu değistirmemesi, yani ısıl kararlı olması istenmektedir.

Polimerlerin ısıl iletkenliklerinin arttırılması amacıyla uygulanan farklı yöntemler vardır. Bunlardan birisi, üretim esnasında polimerlere ısıl iletkenliği yüksek olan tanecik veya lifler katılmasıdır. Bu tanecik katkıları sayesinde polimerin ısıl iletkenliği artmaktadır. Polimerik nanokompozitlerde takviye malzemesi olarak yaygın bir sekilde kullanılan malzemelerden birisi kildir. Kil, tabakalı yapısı, doğada bol miktarda ve ucuz olarak bulunabilmesi gibi avantajlarından dolayı çok tercih edilmektedir. Tabakalı yapıda olan kil mineralleri polimer içinde dağıtılabilme özelliği nedeniyle çok iyi katkı malzemesi olmaktadır.

Bu çalışmada prepolimerik yapıda bulunan poliüretan içerisine halloysit, sepiyolit, ham ve aktifleştirilmiş bentonit nano katkıları eklenerek nanokompozit yapı oluşturulması ve bu nano katkıların poliüretan yapı içerisindeki davranışlarının araştırılması amaçlanmıştır. Çalışmanın temeli nano katkıların farklı yüzdeler ile prepolimerin içerisine katılarak, katalizör varlığında kürleştirilmesine dayanmaktadır. Halloysit, poliüretan prepolimeri içerisinde 4 farklı yüzdede

çalışılmıştır; %3,6, %7,0, % 10, %13. Aktifleştirilmiş bentonit ve sepiyolit %3,6, %5,3, %7,0 oranlarında ve ham bentonit ise %5,3, %7,0, %10, %13 oranlarında kullanılmıştır. Ayrıca kil katkılarının etkilerini karşılaştırmalı olarak görebilmek için poliüretan prepolimeri tek başına da kürleştirilmiştir. Bu doğrultuda 15 adet örnek hazırlanmış ve sonuçlar fiziksel, termal ve mekanik olarak gözlemlenmiştir. Numunelerin karakterizasyonunda FTIR, TGA, Mekanik Test Cihazı ve XRD analizlerinden yararlanılmıştır.

Çalışma sırasında öncelikle kil mineralleri 1 saat boyunca toluen içerisinde bekletilmiştir. Bunun amacı kilin şişmesini tabakalarının belirginleşmesini sağlamaktır. Sonrasında toluen – kil karışımları, poliüretan prepolimeri içerisine eklenmiş ve karışımın sıcaklığı ısıtıcı yardımıyla 80ºC'ye getirilmiştir. Karışımın sıcaklığı 80ºC'ye geldiğinde katalizör, poliüretan-kil-toluen karışımına eklenerek 2 dakika boyunca manyetik karıştırıcı ile karıştırılmıştır. 2 dakika sonunda karışım bir kalıba dökülerek 80ºC'ye ısıtılmış vakumlu etüve konmuştur. 4 saat sonunda örneklerin kürleme işlemi gerçekleşmiş ve vakum etüvden alınarak 1 saat boyunca da desikatörde bekletilmiştir. 1 saat desikatörde bekleme işleminden sonra elde edilen poliüretan-kil nanokompozitlerin (PUNK) analiz işlemine geçilmiştir.

FTIR analizi 500-4000 $cm^{-1}$ spektrum aralığında yapılmıştır. Tek başına kürleştirilmiş olan poliüretan numunesinde tüm karakteristik PU pikleri elde edilebilmiştir. Halloysit, sepiyolit, aktifleştirilmiş ve saf bentonit eklenerek kürleştirilmiş olan poliüretan numunelerinin FTIR analizlerinde ise kil ilavesinin en yüksek olduğu örneklerde spesifik poliüretan spektrumlarının belli oranlarda yer değiştirdiği gözlemlenmiştir.

XRD analizi, hazırlanan kil/poliüretan nanokompoziti içerisinde bulunan killerin kürlenme esnasında tabakalarının açılma derecesini gözlemlemek amacıyla yapılmıştır. Analiz sonuçları, hazırlanan sepiyolit/poliüretan nanokompozit yapının içerisindeki kil tabakalarının açabildiğini göstermiştir. Hazırlanmış olan halloysit/PU, aktifleştirilmiş bentonit/PU ve ham bentonit/PU nanokompozit yapılarında ise bir tabaka açılması gözlemlenmemiştir. Tabaka açılmasının gözlenmemesinin de nanokompozit yapılar oluşurken meydana gelen çapraz bağlanmadan kaynaklı olduğu sonucuna varılmıştır.

TGA analizleri 0-800ºC aralığında yapılmıştır. TGA analiz sonuçlarına göre çalışılan tüm kil çeşitlerinin, poliüretan kompozitin bozunma sıcaklığına olumlu etki ettiği anlaşılmıştır. Artan miktarda halloysit, sepiyolit, ham ve modifiye bentonit katkılarının poliüretanın bozunma sıcaklığını daha da yükselttiği gözlemlenmiş ve ayrıca her bir kil yapısının birbiri ile karşılaştırılması da yapılmıştır. Poliüretan içerisine eklenmiş sabit %7.0 oranında halloysit, sepiyolit, ham ve modifiye bentonit incelendiğinde; saf poliüretan polimerinin bozunma sıcaklığı olan 450ºC'yi halloysit 515ºC'ye, sepiyolit 525ºC'ye, ham bentonit 495ºC'ye, aktifleştirilmiş bentonit ise 500ºC'ye ötelemiştir. Bu sonuçlar sepiyolitin ve halloysitin çalışılan diğer kil türlerine göre daha iyi performans gösterdiğini ortaya koymuştur.

Yapılmış olan mekanik test sonuçlarına göre; polimerik poliüretan yapının içerisindeki halloysit miktarı arttıkça kopma mukavemetinin, kopma anındaki uzama değerlerinin ve elastikiyet modülünün arttığı gözlemlenmiştir. Kompozit yapının içerisine sepiyolit eklenmesi kopma mukavemetinin ve kopma anındaki uzama değerlerinin artmasını sağlamıştır ancak artan sepiyolit yüzdesi bu değerlerin az miktarda azalmasına neden olmuştur. Sepiyolit katkısı polimerik yapının elastikiyet modülüne etki etmemiştir. Ham bentonit katkısı, polimerik poliüretanın elastikiyet

modülünü arttırmış ancak kopma mukavemetine ve kopma anındaki uzama miktarına etki etmemiştir. Polimerik kompozitin içeirsine modifiye edilmiş bentonit katkısı kopma mukavemetini ve kopma anındaki uzama miktarını arttırmıştır ancak elastikiyet modülünde bir değişiklik gözlemlenmemiştir.

Genel olarak sonuçlar incelendiğinde, polimerik poliüretan yapılarına inorganik kil katkısının polimerik yapıya ait termal, mekanik ve kimyasal özellikleri olumlu olarak etkilediği gözlemlenmiştir.

## 1. INTRODUCTION

The discovery of polyurethane (PU) dates back to the year 1937 by Otto Bayer and his co-workers at the laboratories of I.G. Farben in Leverkusen, Germany. The initial works focussed on PU products obtained from aliphatic diisocyanate and diamine forming polyurea, till the interesting properties of PU obtained from an aliphatic diisocyanate and glycol, were realized. Polyisocyanates became commercially available in the year 1952, soon after the commercial scale production of PU was witnessed (after World War II) from toluene diisocyanate (TDI) and polyester polyols. In the years that followed (1952-1954), different polyester-polyisocyanate systems were developed by Bayer [1].

Polyurethanes continue to be one of the most versatile of all polymers, finding applications in foams (flexible, rigid, and in-between), elastomers, coatings, sealants, adhesives, paints, textiles, and films. This volume presents some of the major advances in polyurethanes, both from the materials and research side of things as well as processing and applications, and includes studies on foams (additives, vacuum panel applications, blowing and processing), elastomers, adhesion behaviour and new urethane raw materials [2].

Most polyurethanes are thermoset materials; they cannot be melted and reshaped as thermoplastic materials. Once the reactions have ceased the thermoset polyurethanes are cured and cannot be heat shaped without degradation. The thermal stability results from the croslinking degree of polymer chains (the crosslink density) and from the nature and frequency of repeating units within the polymer chains. Thermoplastic polyurethane elastomers are polymers that bridge the gap between rubbers and plastics. They can be used in a wide range of properties, from hard rubbers to soft engineering thermoplastics as they are elastic and melt-processable. They can be processed on extrusion as well as injection, blow and compression molding equipment. They can be vacuum-formed or solution-coated and are suited for a wide variety of fabrication methodologies. They provide a considerable number

of physical property combinations: high resilience, good compression set, resistance to abrasions, tears, impacts, weather, and even hydrocarbons [3].

The field of nanotechnology is one of the most popular areas for current research and development in all technical disciplines. This obviously includes polymer science and technology and even in this field the investigations cover a broad range of topics. This would include microelectronics (which could now be referred to as nano electronics) as the critical dimension scale for modern devices is now below 100 nm. Other areas include polymer-based biomaterials, nanoparticle drug delivery, mini emulsion particles, fuel cell electrode polymer bound catalysts, layer-by-layer self-assembled polymer films, electrospun nanofibers, imprint lithography, polymer blends and nanocomposites [4].

Polymers are traditionally reinforced with inorganic fillers to improve their properties as well as to reduce costs. These conventional fillers include talc, calcium carbonate, fibers, etc. The achievement of a significant improvement in the composite properties often requires incorporation of a large amount of the filler in the polymer materials, which consequently leads to the loss of transparency of the composites, as well as increase in the bulkiness of the composite materials. Such particulate filled polymers are often classified as microcomposites, based on the dimensions of the phases involved [5]. The commonly used layered silicates for the preparation of PLS nanocomposites belong to the same general family of 2:1 layered- or phyllosilicates. Their crystal structure consists of layers made up of two silica tetrahedral layers fused to an edge-shared octahedral sheet of either aluminium or magnesium hydroxide. The layer thickness is around 1 nm and the lateral dimensions of these layers may vary from 30 nm to several microns and even larger depending on the particular layered silicates [6].

In this study, effects of clay mineral additives on the polyurethane were examined. Polyurethane nanocomposite materials were prepared with the addition of different types of clay minerals such as halloysite, bentonite and sepiolite. Clay minerals were added in different percentages. The properties of the prepared nanocomposites were determined structurally, mechanically and thermally.

## 2. POLYURETHANE

### 2.1 Polyurethane Chemistry

Polyurethanes are composed of reaction with different types of isocyanate and a polyol in the presence of additives and catalysts. Moreover, an ordinary polyurethane may consist of ester, amide, ether, and urea groups other than urethane groups.

According to appropriate combining of beginning raw materials, polyurethanes diversify the different structure, such as flexible, foam, rigid etc. Furthermore, molecular polyurethane structures diversify to based on degree of crosslinking or branching and the amount of chain length.

Polyurethanes create the most versatile polymer group. Production of polyurethane is in extensive range of crosslink densities and stiffness. Structure of PU can vary from very soft to very hard [7].

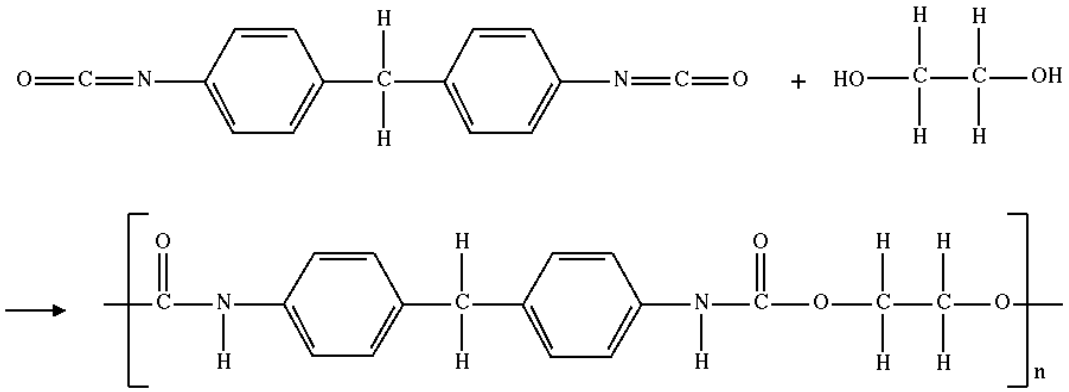

**Figure 2.1 :** Polyurethane reaction [15].

#### 2.1.1 Hard – soft segment theory

With respect to hard – soft segment theory, polimeric polyols form the soft segment and diidoscyanate chains, which is expanded with different type diol and amine

structures, form the hard segments. Hard domain which, constitudes regular polyol (rubbery) phase, are plastic-like fields. However sometimes it can be moderately crystalline structure.

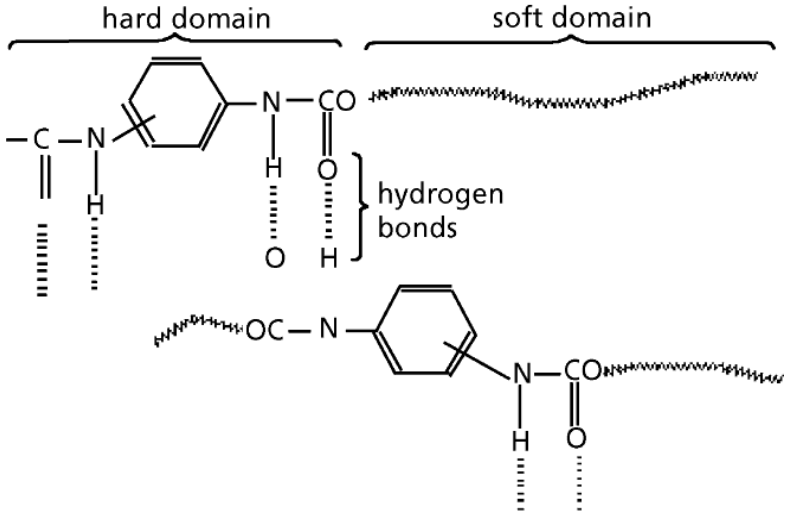


**Figure 2.2** : Hard - soft segments [15].

Hard segments are generated with two different method;

- Urea-plastic phase production is based on isocyanate-terminated prepolymer and water reaction.

- Chain extenders (diols and diammines) and polyisocyanate reactions.

Hydrogen bonds, which are between hard segments's polar group, are moderately substantial for polyurethane. This type of bonds behaves like filler particles and they provide secondary bond forces. Soft segments's polar groups have less degree interaction forces. Surface tension, frictional properties, miscibility and solubility properties of polyurethane can be explained with forces, which are dipole, dispersion, induction and van der Waals forces.

Hard and soft segment domains induce the phase separation, because of thermodynamic inconsistency. Thermodynamic inconsistency leads to nonuniform structure. Hard segment domains are diffused in a soft segment matrix.

General advantages and disadvantages of hard segments;

*Advantages:* Raising of tensile and overlap strength, increasing hardness and stiffness, raising of peel strength, good impact properties at low temperatures, well modulus properties at mild temperatures.

*Disadvantages;* Lower thermal stability, lower overlap shear strength in comparison with reverse morphology [8].

### 2.2 Raw Materials

Various types of raw materials were used in polyurethane synthesis, such as aliphatic & aromatic isocyanates, polyols, chain extenders, catalysts, solvents and plasticisers. Petroleum, coal, salt, air and renewable natural materials are the main sources of raw materials, as shown in figure [7].

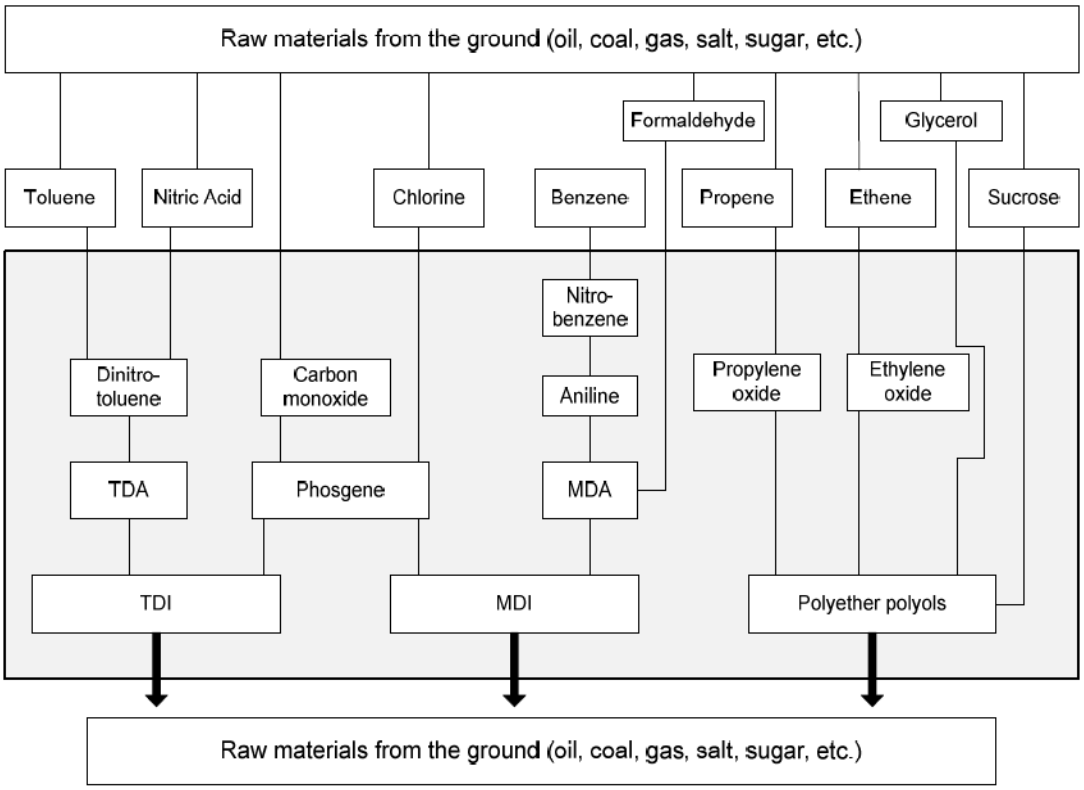


**Figure 2.3 :** Main sources of raw materials [7].

#### 2.2.1 Isocyanates

Isocyanates which contain two or more than two – NCO groups per molecule, are the basic components for polyurethane synthesis. These type of ısocyanates are polycyclic, aliphatic, cycloaliphatic or aromatic in nature. For instance, MDI, TDI, xylene diisocyanate (XDI), hydrogenated xylene diisocyanate (HXDI), 4,4'-dibenzyl diisocyanate (DBDI), isophorone diisocyanate (IPDI) etc [8].

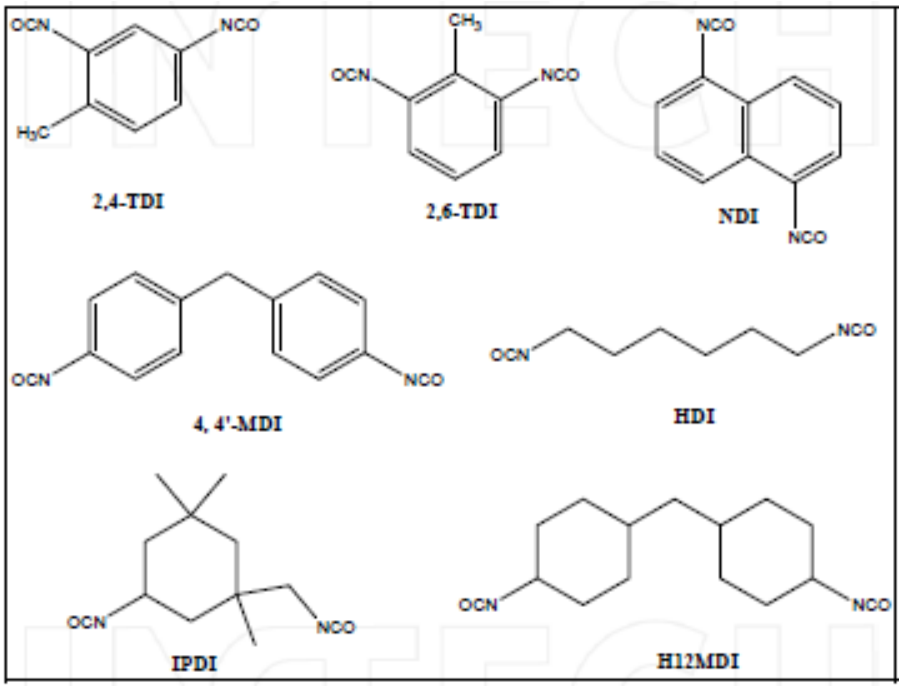


**Figure 2.4 :** Basic isocyanates [39].

### 2.2.1.1 Basic reactions of isocyanates

Primary reaction of producing urethane is the reaction of isocyanate types with hydroxyl groups.

Active hydrogen compounds's nucleophilic centre, assault the electrophilic carbon atom and the hydrogen atom reacts with the –NCO group's nitrogen atom. Aliphatic isocyanates (R = alkyl) are less reactive than aromatic isocyanates (R = aryl) [7].

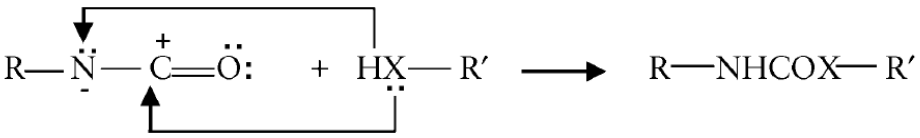


**Figure 2.5 :** Reaction of isocyanate with $H^+$ [24].

There are four basic reaction to produce polyurethane from isocyanate.

*Reaction of isocyanates with alcohols;* for the formation of high molecular weight polyurethane products, active polyfunctional hydrogen chemicals are reacted with isocyanates. Isocyanate – alcohol reactions, which progress at ambient temperatures, are exothermic. Additionally, this type of reaction does not need use of catalyst [8].

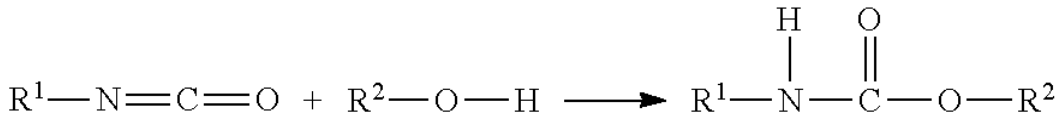

**Figure 2.6 :** Reaction of isocyanate with $OH^-$ [40].

*Reaction of isocyanates with water;* the product of isocyanate – water reaction is unstable carbamic acid which decomposes primary amine and gaseous carbondioxide. In this reaction, two moles isocyanate reacts with one mole $H_2O$, so much more exothermic than isocyanate-alcohol reaction [8].

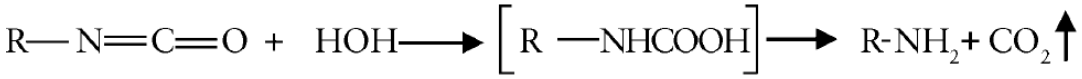

**Figure 2.7 :** Reaction of isocyanate with $H_2O$ [24].

*Reaction of isocyanates with amines;* Amine – isocyanate reaction product is urea. Reaction occurs in 0-25°C. Primary amines are more reactive than aromatic amines and secondary aliphatic amines [8].

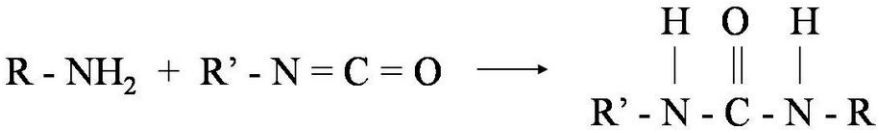

**Figure 2.8 :** Reaction of isocyanate with amine [40].

*Reaction of isocyanates with urea and urethane groups;* -N-H groups, which is involved in urea structure, react with the isocyanate and an *biuret* is occurred [8].

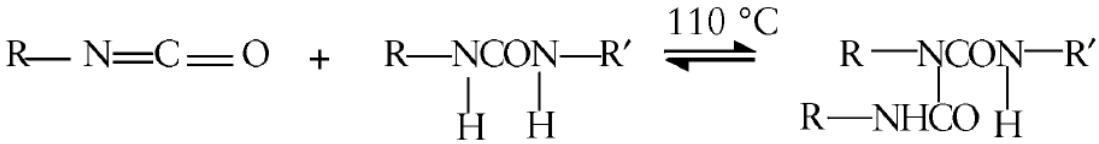

**Figure 2.9 :** Reaction of isocyanate with urea [24].

Hydrogen atom, which is attached to nitrogen atom in –NCO, reacts with the isocyanate and *an allophanate* is occurred.

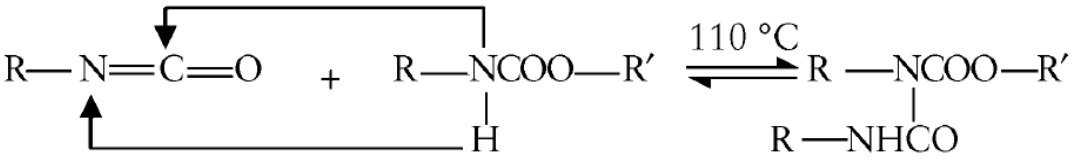


**Figure 2.10 :** Reaction of isocyanate with urethane [24].

### 2.2.1.2 Types of isocyanates

*Aromatic isocyanates;* the most commonly used and known aromatic diisocyanates are TDI (toluene diisocyanate) and MDI (Methylene diphenyl diisocyanate). TDI, which is manufactured from toluene, has no color and low viscosity liquid at 25°C.

The other monomer MDI, which has low vapour pressure and no color, is crystalline solid at 25°C [7]. Rigid and semi-rigid polyurethane foams which are produced from MDI type isocyanate, are used in insulation, footwear, coating, adhesive and elastomer sectors.

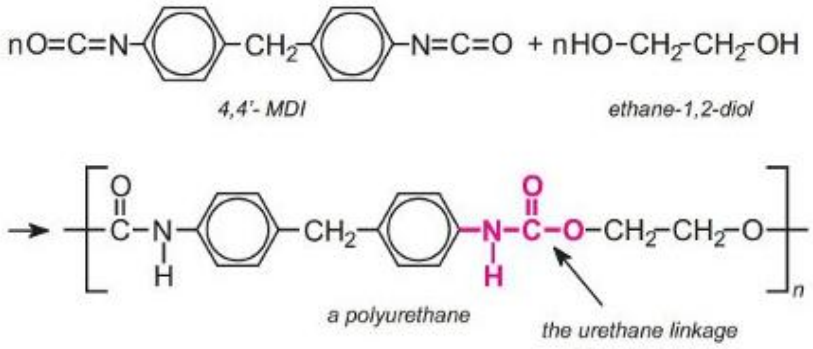


**Figure 2.11 :** Polyurethane synthesis from MDI [10].

TDI is used to produce polyurethane foams, which have flexible properties. Household linens and furniture industries use these types polyurethane foams [8].

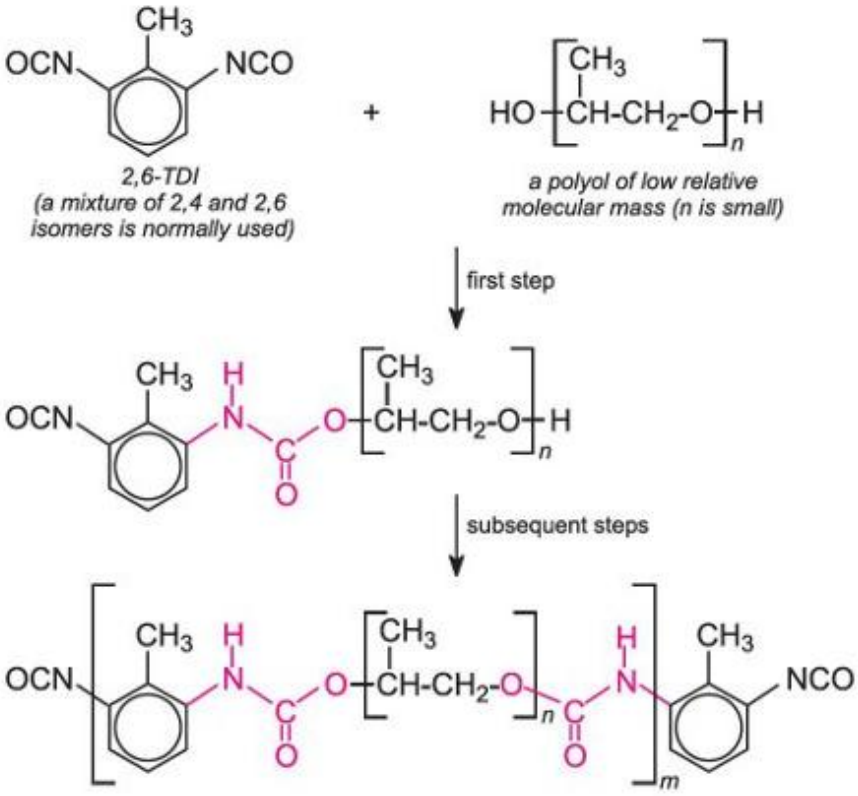


**Figure 2.12 :** Polyurethane synthesis from TDI [10].

*Aliphatic isocyanates;* The most extensively used and known aliphatic diisocyanates are HDI (Hexamethylene diisocyanate), IPDI (Isophorone diisocyanate), $H_{12}$MDI (Dicyclohexylmethane-4,4'-diisocyanate).

HDI is manufactured from reaction of hexamethylene diamine (HDA) and phosgene. Its freezing temperature is 55°C and it is fluid at 25°C.

IPDI is another type of aliphatic isocyanate. Formation of IPDI is based on the reaction of isophorone and HCN reaction. After amination of cyanoketone, isophorone diamine (IPDA) is formed. Finally, isophorone diamine (IPDA) is reacted with phosgene and IPDI production occurs. IPDI is fluid at room temperature.

Hydrogenated MDI is named $H_{12}$MDI. Hydrogenated MDA (Methylene dianiline) and phosgene react each other and $H_{12}$MDI is formed. Melting point of this chemical is 19-23°C, consequently $H_{12}$MDI is fluid at room temperature. Commercial use of this product is several mixtures of trans-trans cis-trans and cis-cis isomers [9].

### 2.2.2 Polyols

Second basic raw material for polyurethane production is polyol. A polyol is an alcohol, which is containing multiple hydroxyl groups. Polyols are examined two groups;

First group of polyols have monomeric structure and low molecular weight (MW), such as dipropylene glycol, propylene glycol, ethylene glycol, diethylene glycol, 1,4 butanediol, triethanolamine, glycerol, etc. They are used as initiator for monomeric polyol production. The other group of polyols contains low molecular weight polymers. Moreover they involve terminal hydroxyl groups; hydroxy telechelic oligomers. Polimeric polyols, which are called oligo-polyols, characterised by $M_n$ (average molecular weight) and MWD (molecular weight distribution) [6].

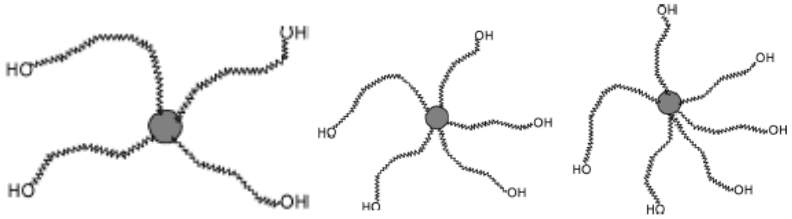

**Figure 2.13 :** General structure of a tetraol, pentol, hexol (oligo-polyol) [6].

#### 2.2.2.1 Types of polyols

Polymeric polyols are usually polyethers or polyesters polyols. Other commercial polyols are polycarbonate polyol, polycaprolactone polyol etc.

*Polyether polyols,* which have most conventional usage in industry, compose the main structure of polyurethane. Polyether polyols are manufactured by alkali-catalyzed polymerization technic. Reaction occurs between difunctional or polyfunctional polyols and epoxide groups (ethylene / propylene oxide) [7].

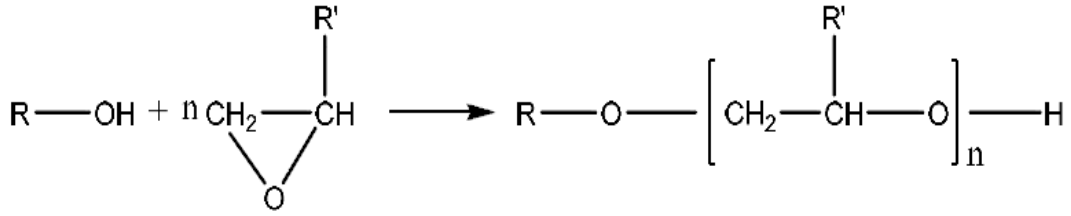

**Figure 2.14 :** Polyether polyol synthesis [7].

Polyurethane properties can be regulated with length of polyether chains and initiator's functionality factor. Dipropylene glycol (f:2) and glycerine (f:3) are low functionality initiators. This type of initiators are used in nonrigid/flexible polyurethane applications. Sucrose (f:8), sorbitol (f:6) and toluenediamine (f:4) are high functionality initiators and they are used in polyurethane applications which are rigid form [7].

**Table 2.1 :** Polyether polyol initiators [7].

| Functionality | Initiator |
|---|---|
| Functionality 2 | Propylene gylcol, Ethylene glycol, Water, Methyldiethanolamine |
| Functionality 3 | Glycerol, Trimethylolpropane, 1,2,6-Hexanediol, Triethanolamin, PhosphoricAcid |
| Functionality 4 | Pentaerythritol, Methyl glycoside, Ethylenediamine, Toluenediamine |
| Functionality 5 | Diethylene triamine |
| Functionality 6 | Sorbitol |
| Functionality 8 | Sorbitol Sucrose |

*Polyester polyols* have two main groups for polyurethane; aliphatic and aromatic polyesters. This type of polyols are used the low amount of use in comparison with polyether polyols. Production process of polyester polyols are more costly and product specifications and properties ensure disadvantages; such as high viscosity, low photo-oxidation sensitivity etc. Aliphatic polyesters are synthesized by polycondensation reaction of functional dicarboxylic acids, for instance adipic acid, phthalic acid, sebacid acid and hydroxyl component, for instance ethylene glycol, propylene glycol, diethylene glycol, 1,4-butanediol etc [7].

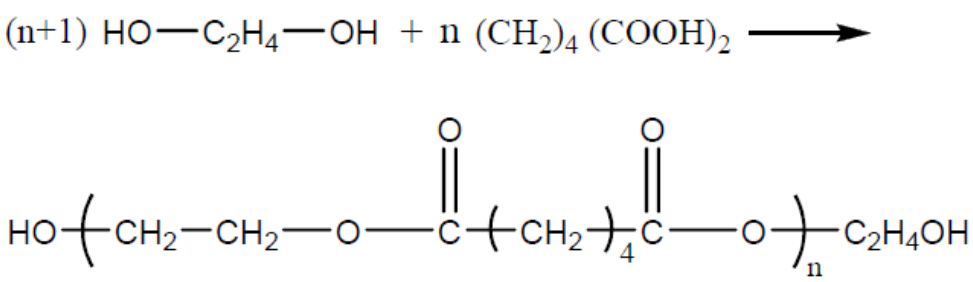

**Figure 2.15 :** Aliphatic polyester synthesis (polyethylene adipate) [7].

Aromatic polyesters are synthesized by trans-esterification reaction of polyethylene terephthalate (PET) which is recycled. This polyol's functionality is 2 and its colour is deep. It is used for rigid formed polyurethane foams.

In brief, polyether polyols have more advantages than polyester polyols;

Variety of functionality can change between 2 and 8.

The product is more fluid than those of polyesters.

Manufacturing costs are much lower than aliphatic polyester types.

Polyurethane foams have hydrolysis resistant property [7].

Other types of polyols are graft polyols, polyurea polyols, polycarbonate polyols, hydantoin-containing polyols, polyolefinic polyols.

*Graft polyols are* produced by acrylonitrile and styrene reaction with free radical vinyl copolymerization technic. They increase the hardness property of foams and elastomers.

*Polyurea polyols* are synthesized by an amino-polyol and an isocyanate reaction with polyaddition technic. Usage area of this type polyol is semi-rigid foams [7].

*Polycarbonate polyols* are manufactured by diethyl/dimethylcarbonate and different type of diols polycondensation reaction. Especially, 1,6-hexanediol is mostly used production of polycarbonate polyols [9].

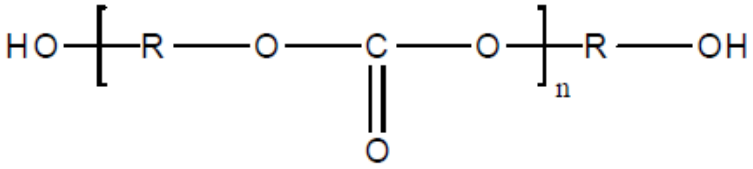


**Figure 2.16 :** Polycarbonate polyol [7].

### 2.2.3 Additives

In polyurethane production, addition to the use of isocyanates and polyols, different types of additives can be used for various application areas. Some of additives are added synthesis reaction, some of them are used in formulations. Basic additives are crosslinking agents/chain extenders, catalysts, plasticizers, solvents, surfactants, blowing agents for foams, flame retardants, fillers, antioxidants, release agents for mouldings and colorants [7].

### 2.2.3.1 Chain extenders and cross linkers

In polyurethane production, crosslinking agents (f:2) and chain extenders (f:3 or greater) are frequently used materials. These additives are low molecular weight diamines, diols or triols. Butanediol, glycerol or trimethylolpropane type di- and polyhyric alcohols are added to reaction as crosslinking agent/chain extender for OH. Because of steric hindrance, $NH_2$ groups which is involved in aromatic diamine structure, react with NCO groups slowly. Therefore, aromatic diamines are used as $NH_2$ crosslinking agents/chain extenders. Moreover cumyl peroxide can be a MDI polyurethane. Using crosslinking agents/chain extenders provide to check polyurethane polymer's network density [7].

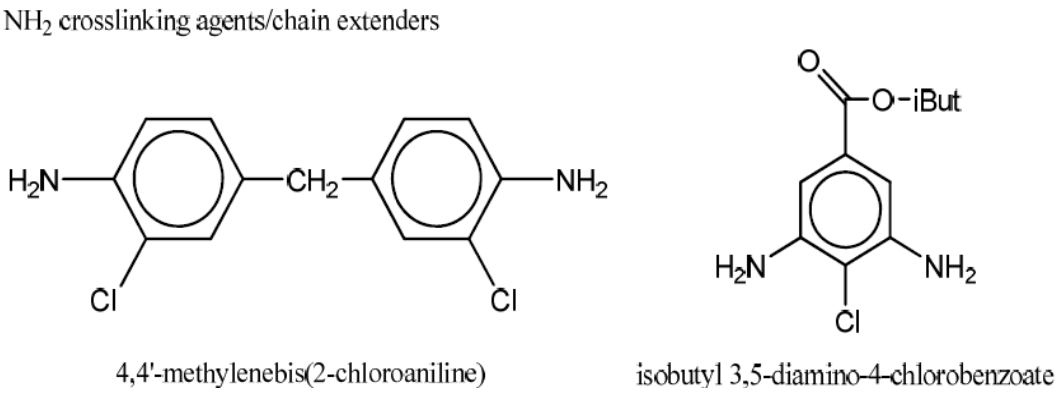


**Figure 2.17 :** $NH_2$ crosslinking agents/chain extenders [7].

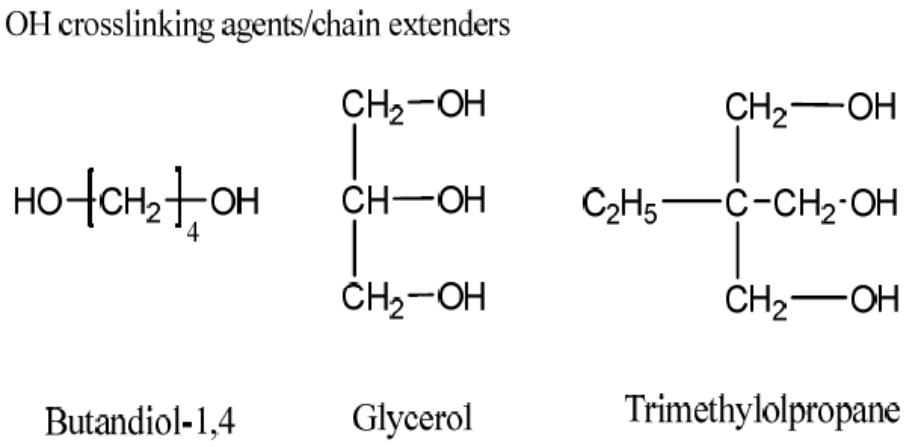


**Figure 2.18 :** OH crosslinking agents/chain extenders [7].

#### 2.2.3.2 Catalysts

Tertiary amines are most frequently used catalysts in polyurethane production. Isocyanates reactions are activated by these type of catalysts at mean temperatures, for instance carboxylic acids, alcohols, water etc. Though, for high temperatures tertiary amine type catalysts are not strong enough, so strong base catalysts, which are NaOH, NaOR etc., are used for this temperature conditions.

Metals, which are in the form of organic acid salts or/and organometalics increase the formation of urethane linkage. Dibutyl tin dilaurate and tin (II) octoate, which are tin compounds, are in special very efficient components.

Moisture cure catalysts can be used different areas, especially in adhesive applications;

- Tin catalysts; DBTDA (dibutyltin diacetate), DBTDL (dibutyltin dilaurate);
- Amines; tertiary amines, morpholine derivatives;
- Bismuth catalysts;
- Mercuric catalysts [11].

#### 2.2.3.3 Other additives

*Solvents* decrease the fluidity of formulations and provide wetting property to substrate. Nowadays, different industrial sectors are trying to reduce solvent usage in polyurethane products. Recommended solvent usage is lower than %10. General solvents types are;

odourless mineral spirits;

xylene;

solvent naphtha;

mineral spirits;

glycol ether acetates [11].

*Plasticizers* which enhanced polyurethane polymer's free volume, do not manufacture complete solvation. Plasticizers decrease the glass transition

temperature and change the sealants's curing characteristics. General plasticizers using in PU sealants;

- hydrocarbon extenders;
- dipropylene glycol dibenzoate;
- diundecyl phthalate (DIDP);
- dioctyl phthalate (DOP) etc [11].

*Flame retardants:* Polyurethane foams, which have flexible, rigid and semi-flexible types, are instinctively flammable materials. Using flame retardants in polyurethane foams aim decreasing the fire formation possibility, in short deactivate the cumbustion cycle. Combustion mechanism are shown in Figure 2.19.

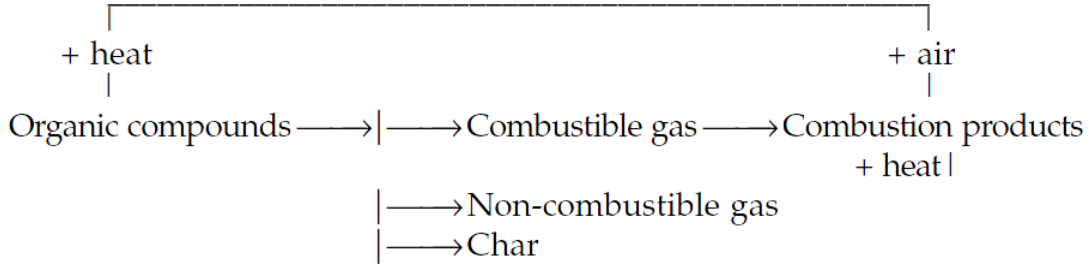


**Figure 2.19 :** Combustion cycle [11].

In industry, different types of flame retardents are used by various sectors, such as liquid, powder, radical scavenger, nonreactive, reactive, char-forming, noncalorific additives [11].

*Antioxidants:* Manufacturing low density polyurethane is main aim for foam industry. Antioxidants provide to product low density PU. In addition, antioxidants prevent formation of burning in production of flexible polyurethane. Antioxidants types for polyurethane foams;

primary antioxidants; Hindered phenol, BHT,

secondary antioxidants; Phosphite, thioether [11].

*Colorants:* In industry, certain applications necessitate to product colored foams. For this reason, spirit soluble dyes and pigment dispersions are added flexible polyurethane foam productions [11].

## 2.3 Polyurethane Product Types

### 2.3.1 Rigid foams

Rigid polyurethane foams, which include closed cell at very high percentages, have different characteristics. For instance;

-Foams can be producted at room temperatures, no need heat.

-Foams are used with different types of materials; fibers, steel, thermosetting resins and foams, woods etc.

-Foam density range can be change at wide values.

-They are capacitance to petroleum products, oils and non-polar solvents.

-With low density foams provide thermal insulation features.

Rigid polyurethane foams, which are used for the subscribing energy saving in the world, are implemented in many thermal insulation products such as refrigerators, freezers, refrigerated trucks, refrigerated containers, refrigerated warehouses, building and construction, chemical and petrochemical plants, water heaters, portable ice boxes, and thermos bottles [11]. Furthermore, horticulture, furniture and sports equipment, solar technology and rock consolidation in mining and civil engineering sectors use the versatile rigid PU foams [7].

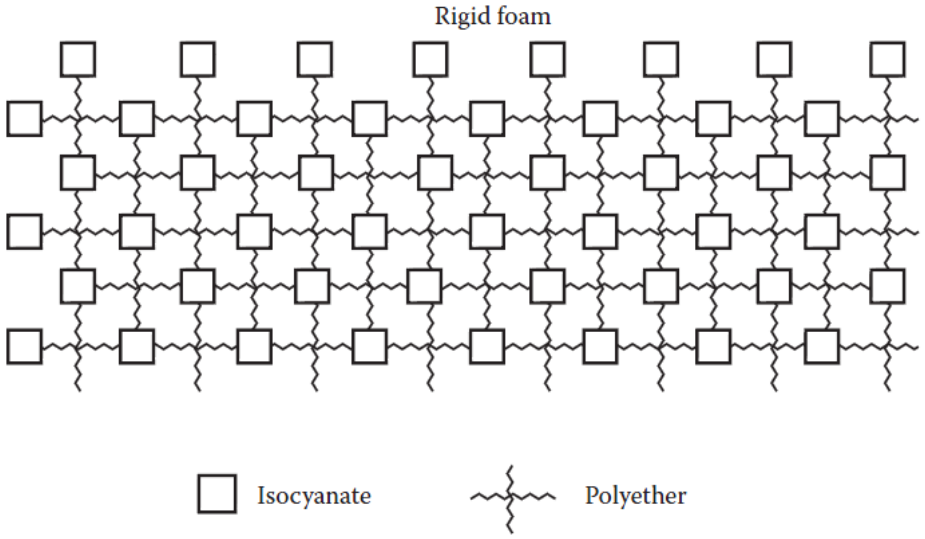


**Figure 2.20 :** Highly crosslinked/closed cell rigid foam structure [12].

### 2.3.2 Flexible foams

Another type polyurethane is flexible & semi- flexible foams. Polyurethane manufacturers generate low-density foams, which have essentially high-strength, bubble-free elastomeric properties. Flexible polyurethanes are produced with two main methods; the blow reaction and the gelation reaction. These reactions ensure open-celled morphology in the polyurethane foam. Open celled morphology is gotten different physical properties to the foam, such as sound insulation, light, durable, supportive and comfort [13].

As well, flexible polyurethane foams are categorized into the process type; slabstockfoams and molded foams. Semiflexible foam, conventional ipolyether foam, super-soft foam, high-resilience (HR) foam, viscoelastic foam, energy-absorbing (EA) foam and flexible polyester foams take part in slabstock foams. Molded foams include hot molded foam and cold molded foam [11].

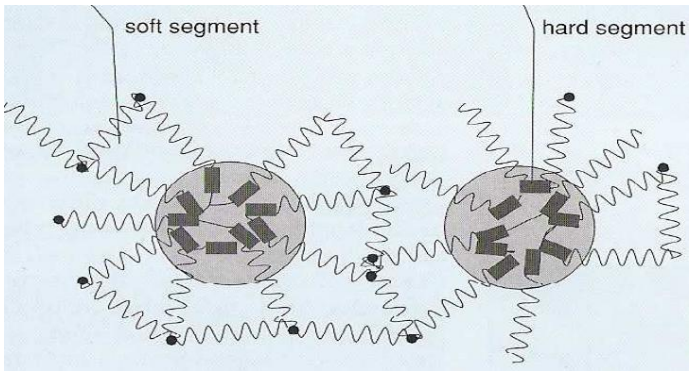


**Figure 2.21 :** Open cell-flexible polyurethane foam structure [7].

### 2.3.3 Thermoplastic polyurethane foams

Thermoplastic polyurethane (TPU) is another class of polyurethane with many different and useful properties.

The structure of thermoplastic polyurethane chains are formed from blocks, which include two types of segments; hard and soft segment.These segments are linked together by covalent bonds and they constitude block copolymer. As mentioned before, hard segments are generated with reaction of the diisocyanate and the short-chain diol. Furthermore, soft segments are formed with reaction of the diisocyanate and the long-chain diol. Hard segments have high density, so they are rigid form. Soft segments have low density, so they are very flexible form.

Unique structure in thermoplastic polyurethane provides many advantages for usage. For instance; very high elasticity,

- good abrasion resistance,
- excellent tear strength,
- very good oil and grease resistance,
- excellent mechanical properties, combined with a rubber-like elasticity,
- outstanding low-temperature performance,
- high transparency, easy to coloring, recyclability etc [4, 13].

Because of these advantages, TPU is used in many different industries. Especially in automotive industry, it is used in aerial mountings, decorative and surround strips to spoilers, snow chains and starting aids, exterior mirror housings, parts for roof racks, slide bearings and automotive body-side moldings, ball joint gaiters, bellows etc. Besides the automotive industry, TPU products are used in sport and leisure sectors [7].

### 2.4 Polyurethane Production Techniques

In industry, three main method are used for production of polyurethane. these methods are one-shot method, prepolymer method and quasi-prepolymer method. Quasi prepolymer means "partial prepolymer". Prepolymer and quasi-prepolymer production technics consist of two step. In one-shot production technic, all raw material inputs are stirred and directly polymerized. However, in prepolymer and quasi-prepolymer technics, polyol and isocyanate inputs are prereacted and constituted prepolymer are mixed with other ingredients in second part. For production of flexible polyurethane are used one-shot method, for producing rigid polyurethane, prepolymer and quasi-prepolymer technics are used.

On the other hand, method selection is subjected to desire specification of product. PU formation is a highly exothermic process. The one-shot method is mainly used with highly viscous component since viscosity will decrease as the amount of heat increased. Patrick Vermette emphasizes that, "for a better control of the temperature, the prepolymer method is more suitable since the total amount of heat will be distributed in two successive steps. For the quasi-prepolymer method, the mixing of

the components is a little different and usually leads to a lower viscosity mixture." [18].

### 2.4.1 Polyurethane prepolymers

Isocyanate groups include high reactivity edges, which is reacted with OH groups. When the OH groups react with the diisocyanate at the whole end, a prepolymer structure are created.

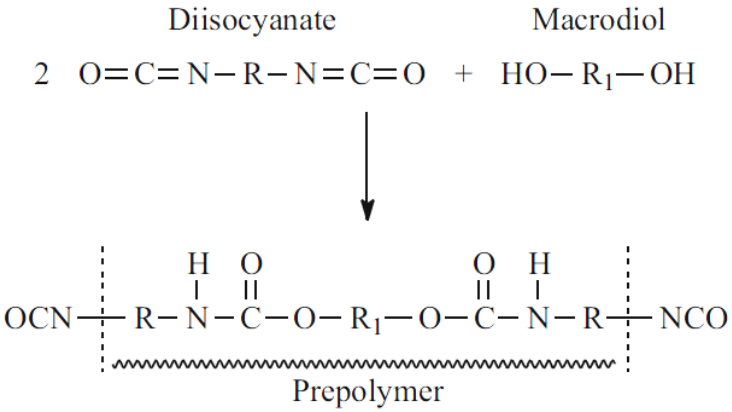


**Figure 2.22 :** Prepolymer formation [15].

As shown in Figure 2.22, prepolymer ends consist of NCO (isocyanate) groups, that are high reactive to form elastomers and foams. Prepolymer products are high viscosity fluids [2].

Prepolymers must be produced under controlled conditions. For protecting the isocyanate and polyol from atmospheric moisture, reaction must be occured in nitrogen athmosphere. Reaction temperature must be higher than 60°C, but not surpass the 90°C definitely. For keeping the viscosity of polyurethane prepolymer at desired range, temperature must be controlled attentively. Because at high temperatures, prepolymer forms viscous. The full-prepolymer systems are used for production of imide and amide foams [16].

Prepolymers are qualified by content of NCO group, solid content, type of isocyanate, polyol type, functionality of polyols weight of molecule, flash point and pressure etc.

Variation of polyurethane are changing according to rate of reaction in prepolymerization reactions. For instance, IPDI and secondary alcohol reaction rate is slightly slow but MDI and primary alcohol reactions occur mild reaction rate. For

high temperature, catalyst must be used for aliphatic prepolymerization. Reaction conditions; temperature is between 80-90 °C, reaction time is nearly 4 hour and use of catalyst amount is 15-30 ppm.

Advantages of using prepolymer production technic for polyurethane manufacturing;

- during polymerization, controlling the polymer structure formation is more easy and provide monotype product for every different batch production,
- decreases the use of different controlling equipment during production,
- provides safety conditions for appreciable steam pressure [17].

### 2.5 Polymer Nanocomposites

Nanotechnology, which is understanding of physical, chemical and biological processes in the nanometer scale, is developed the functional materials, devices and systems to control and produce the new technologies. Nano is an interdisciplinary approach. Last 10 years, it found new application areas which are materials science, mechanics, electronics, optics, medicine, plastics, energy sectors [19].

Polymer nanocomposites are two-component materials, one of them is polymer and the other one is fillers. Polymer structures are strengthened by nanoscale fillers. Fillers concentration, particle size and shape influence the properties of the composite materials [20].

#### 2.5.1 Polymer-clay nanocomposites

Polymer/clay nanocomposites (PCNs) are a new category of chemicals which have appealed more attetion from scientists and engineers because of their advanced and important properties such as high dimensional stability, reduced gas permeability, heat deflection temperature, gas barrier performance, flame retardancy, optical clarity and enhanced mechanical properties when compared with the uncured polymer and micro-macrocomposites [21].

In polymer layered silicate (PLS) nanocomposites, layered silicates have two different characteristics. One of typical property is dispersing ability of silicates into the own layers. The other typical property is consisting of ion exchange reactions with cations in its surface [6].

Structure and chemistry of these layered silicates are provided in Figure 2.23.

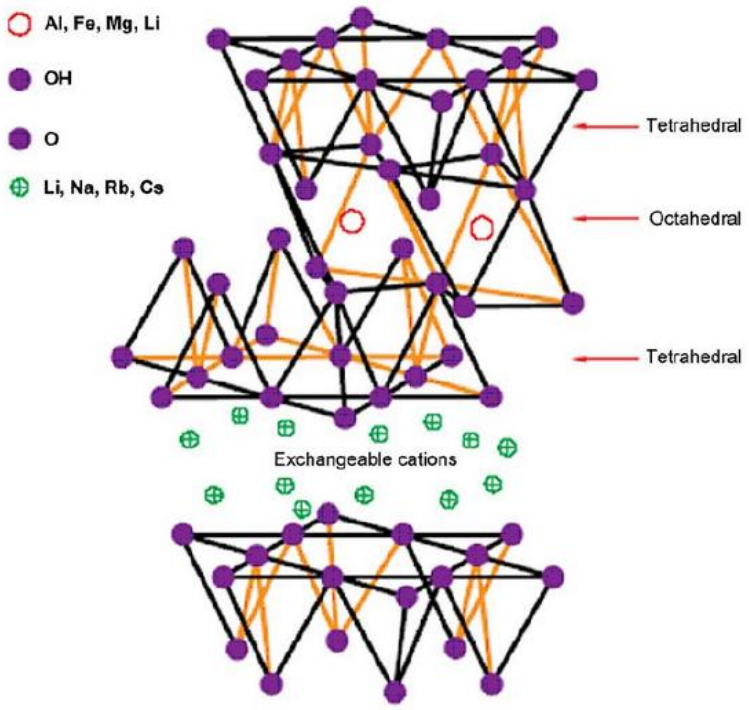


**Figure 2.23 :** Structure of layered silicates [25].

Polymer-clay nanocomposites are accomplished only when silicate layers are broken down individually in polymer matrix as shown in Figure 2.24. In addition, when compared with pristine resins, polymer clay nanocomposites have better mechanical, thermal, flammability and barrier properties. These improvements are achieved by large surface area to volume ratio of well distributed and exfoliated clay minerals [41].

Subjected to interfacial transaction strength between layered silicate and polymer structure, three different types of polymer layered silicate nanocomposite structures are thermodynamically best known:

*Intercalated nanocomposites*: In an intercalated nanocomposite, the intervention of polymer matrix into the layered silicate structure takes place in a crystallographically ordered mode, irrespective of the clay to polymer ratio. Properties of the composite materials characteristically seem these type of ceramic materials.

*Flocculated nanocomposites*: These type of nanocomposites generally resemble intercalated nanocomposites, but layered silicates are occasionally flocculated in consequence of hydroxylated edge-edge interaction of the silicate layers. The

polarity degree of the matrix polymer is of basis importance in controlling the structure of nano material.

*Exfoliated nanocomposites:* In exfoliated nanocomposites, the silicate layers are divided in a polymer matrix by a medial distance. Generally, the clay content of an intercalated nanocomposites are much higher than exfoliated nanocomposite [6].

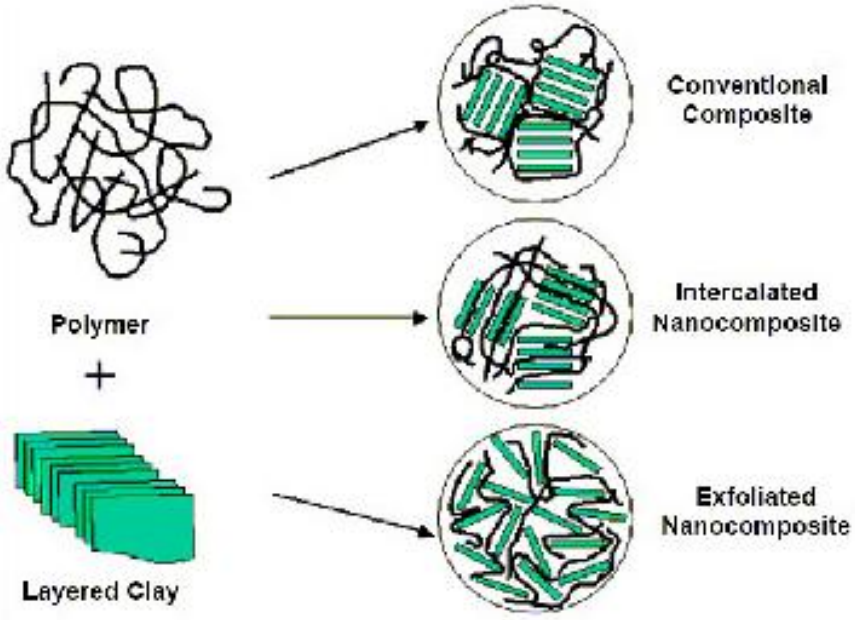


**Figure 2.24 :** Different types of polymer-clay nanocomposites [25]

### 2.5.2 Preparation methods of PLS nanocomposites

There are three main methods for prepare polymer layered silicate nanocomposites;

#### 2.5.2.1 Melt intercalation method

This method includes hot processing, statically or under shear, a mixture of the polymer and layered silicates above the polymers softening point. This method has great advantages over either in situ intercalative polymerisation or polymer solution intercalation methods. First advantage, this method is risk free for environment due to the absence of organic solvents. The other advantage, it is consistent with current industrial manufacturing processes, for instance injection moulding and extrusion. The melt intercalation method provides the use of polymers which were priory not appropriate for the solution intercalation method or in situ polymerisation. This

solvent-free method would rather for practical industrial product manufacturing because of its avoiding environmental risks and high efficiency [6].

#### 2.5.2.2 Intercalation of polymer or pre-polymer from solution

This production method is based on a solvent system, in which the silicate layers are swellable and pre-polymer or polymer is soluble. Firstly, the layered silicate is swollen in a solvent system, for instance toluene, water and chloroform [6].

When the layered silicate and polymer solutions are stirred, the polymer chains intercalate and relocate the solvent within the interlayer of the silicate. Above remove of solvent, the intercalated structure maintains, concluding in polymer layered silicate nanocomposites.

#### 2.5.2.3 In situ intercalative polymerisation method

In this polymerization method, the layered silicates are swollen within the liquid monomer or a monomer solution. In this way the polymer constitution can take place in between the intercalated layers. Polymerisation can be started either by radiation or heat by the diffusion of a suitable initiator, or by an organic initiator or catalyst mixed through cation exchange inside the interlayer before the swelling step by the monomer [6].

### 2.6 Clay Minerals

Clay minerals are the small particled section of geology science. Clays were primarly identified as composed of granules less than 211 m in diameter, beyond the limit of microscopic dissociation. In environment most of clay configurations have a phyllosilicate or layer structure. Such a structure means that particle dimension ratio is a far amount a sheet of paper, in other words, more and more larger and longer than thick structure. Other minerals of different granule images existing in the clay fraction include quartz, zeolites and oxide minerals along with little sections of all of the other minerals found in the geological environment. According to the statistics, clay minerals have a common structure but they are nearly all the while the consequence of chemical changes or thermal alterations in the range of near-surface conditions. The maximum range of temperatures can be given as 4-250°C for the clay mineral formation. At higher temperatures, the layered silicate minerals are

qualified to be of metamorphic source and they have a strong inclination to have a larger granule size than that given to include the clay mineral area. They do not have the same constitution as minerals of lower temperature source [26].

Basic illustrative structure of clay mineral is shown in Figure 2.25.

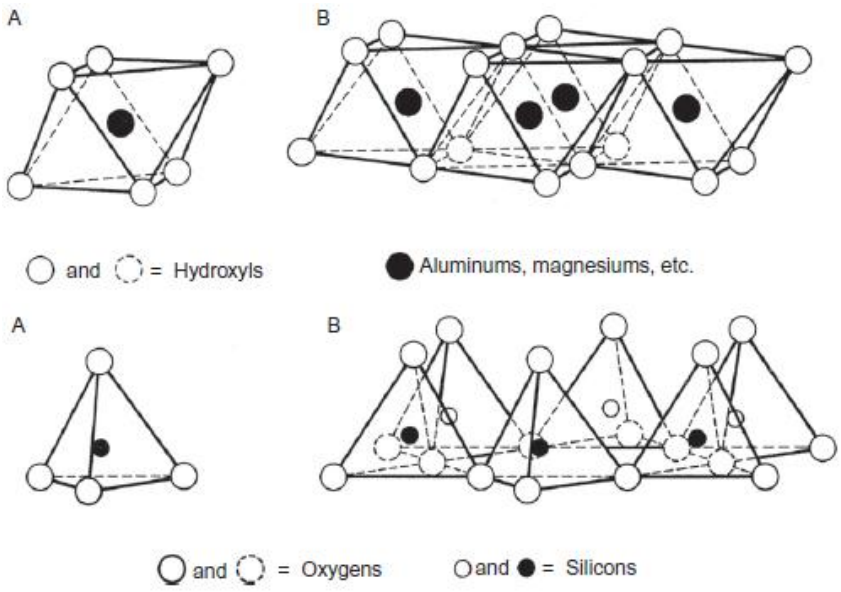


**Figure 2.25 :** Schematic illustration Bottom: (A) a silica tetrahedron in which the central silicon ion is coordinated to four oxygens; (B) a tetrahedral sheet formed by linking silica tetrahedra through corner-sharing. Top: (A) an alumina octahedron in which the central aluminium ion is coordinated to six hydroxyls; (B) an alumina octahedral sheet formed by linking octahedra through edge-sharing [28].

### 2.6.1 Properties of clay minerals

Clays are categorized on the base of their crystal structure and the location and quantity of deficit or excess charges per basic cell. In the content of polymer nanocomposites, the amorphous clays are a huge boredom as they are difficult to suspend from the crystalline clays. The crystalline clays range from kaolins, which are slightly regular in chemical constitution, to smectites, which in large scale diversify in their constitution, cation exchange ability, and the ability to spread. The ease of separation of the unique sheets is related to the interlamellar charge. Clay particles are generally plate-shaped, but some types are tubular or scroll-like. Particular clay particles are nanometre-sized especially in one dimension. Aqueous mixtures of clays which are thixotropic, are sensitive to ion concentration [27].

The structural layer (tetrahedral and octahedral sheets) of clay minerals usually have two different types of charge: structural (or permanent) and surface ( pH dependent). The permanent charge is usually due to ion substitutions, although it can be caused by structural imperfections. Ionic substitution of $Al^{+3}$ for $Si^{+4}$ in the tetrahedral sheets, or $Mg^{+2}$ or $Fe^{+2}$ for $Al^{+3}$ in the octahedral sheets, are the origin for most permanent negative charge in clay minerals [42]

### 2.6.2 Classification of clay minerals

Classification of clay minerals, which is named layered silicates, are shown in Figure 2.26.

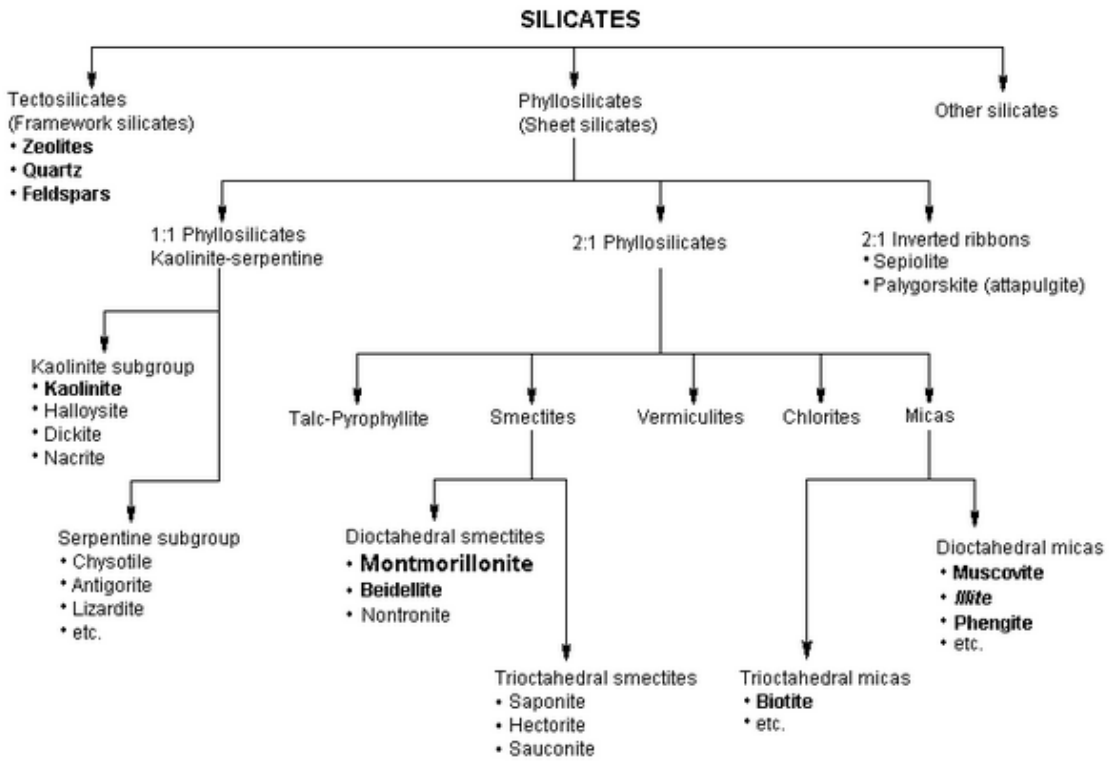


**Figure 2.26 :** Classification of layered silicates/clay minerals [29]

Clay minerals are categorized with depending on their molecular structures and their general formulations. In this thesis, halloysite, bentonite and sepiolite types clay minerals are used.

### 2.6.2.1 Halloysite

As kaolinite, halloysite mineral has the same theoretical structure $SiO_2/Al_2O_3$ ratio. However, water content of halloysite is higher than kaolinite. The completely hydrated type is $Al_2O_3.2SiO_2$ - $4H_2O$, which contains two water layers between conjunctive kaolinite layers resulting in a 10.1 A thick unity. To reduce the water content to $2H_20$ and decrease the thickness to the kaolinite value of 7.1 A. For reduce to water content of halloysite, which is needed to heat at temperature from 200 to 400°C.

Halloysite mineral has a tubular structure with the radial of C axis. Most of halloysites are rather irregularity throughout around the circumference and both of the a and b axes [30].

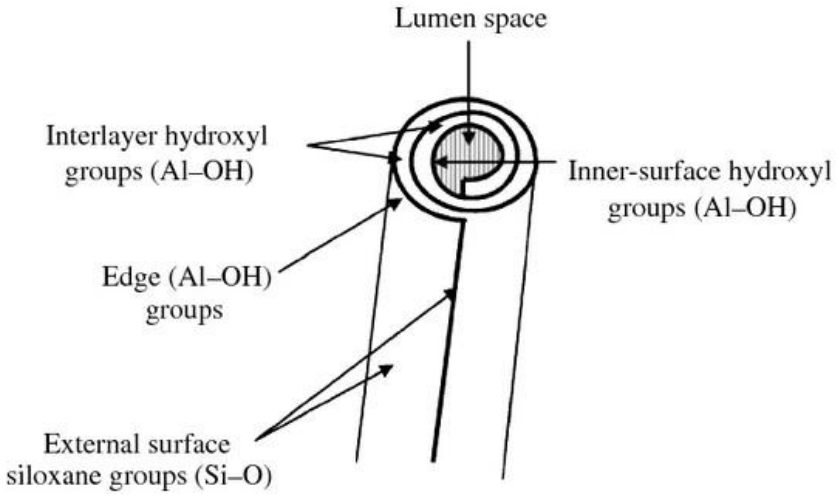


**Figure 2.27 :** Structure of halloysite [31]

Halloysite is used as as nanofillers and in controlled release technology for a range of active agents. Advantages of halloysite nanotubes;

- Eco-friendly, non-toxic, biocompatible
- Small particle size, high surface area and good dispersion
- Higher capacity of cation exchange
- Sustains uniform, maintained release rates
- Capable of prohibiting release unless triggered and tuneable release rates
- Protects active agent within its lumen during harsh material processing

• Capable of loading multiple active agents

• Decreases active agents volume

• Applicable in many area for instance sprays, creams, powders, gels, lotions

• Excellent loading rates to other carriers,

• Rapid adsorption rate and great adsorption capacity

• High aspect ratio, high porosity and non swelling

• Regeneration ability [32].

### 2.6.2.2 Bentonite

Bentonite, whose colour changes from white to yellow, to olive green, to blue to brown, is located in MMT nearly more than 80%. Grades of this mineral show a broad spectrum of properties and as a consequence find a diversity of applications and uses. Its source is a hydrothermal alteration of volcanic ash deposited in a variety of fresh water and marine basins. This origin is categorized by low energy environments and temperate climatic conditions. Main usage areas of bentonite are in foundry sands, iron ore pelletising, drilling muds, absorbents, different type of composite liners, food additive for poultry and domestic animals, foods, in filtration, cosmetics and pharmaceuticals. Bentonite has been used for clearance of liquids, especially white wine and juice. Bentonite is a section of adsorbent, bleaching and catalyst clays [27].

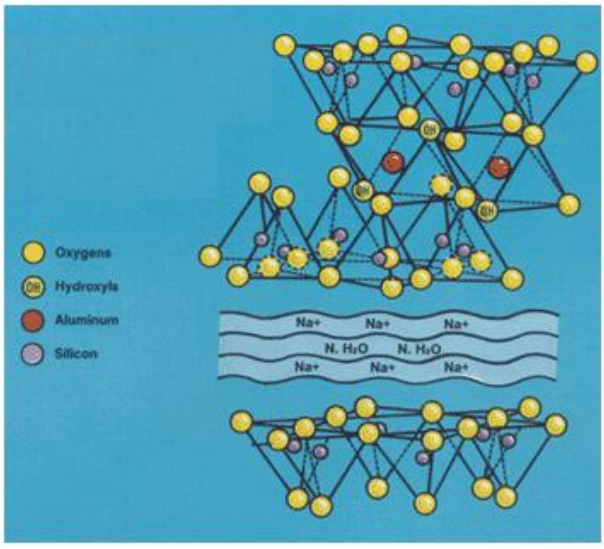


**Figure 2.28 :** Structure of bentonite [33]

### 2.6.2.3 Sepiolite

Sepiolite, which is consisting of magnesium hydrosilicate, is in fibrous structured natural clay mineral. Half-cell formula of sepiolite is $S_{12}Mg_8O_3(OH)_4(H_2O)_4{\cdot}8H_2O$. Its structure is composed of channels and blocks extending along the fiber axis. These channels are filled with zeolitic water. Each block is located between two tetrahedral silica layers in the octahedral center is composed of a layer. Sepiolite is strategic clay mineral because of rheological, sorptif and catalytic properties. It has numerous usage area, especially, due to the superior properties of asbestos fibers are preferred to use in blended cements [35]. Shematic structure of sepiolite is shown in Figure 2.29.

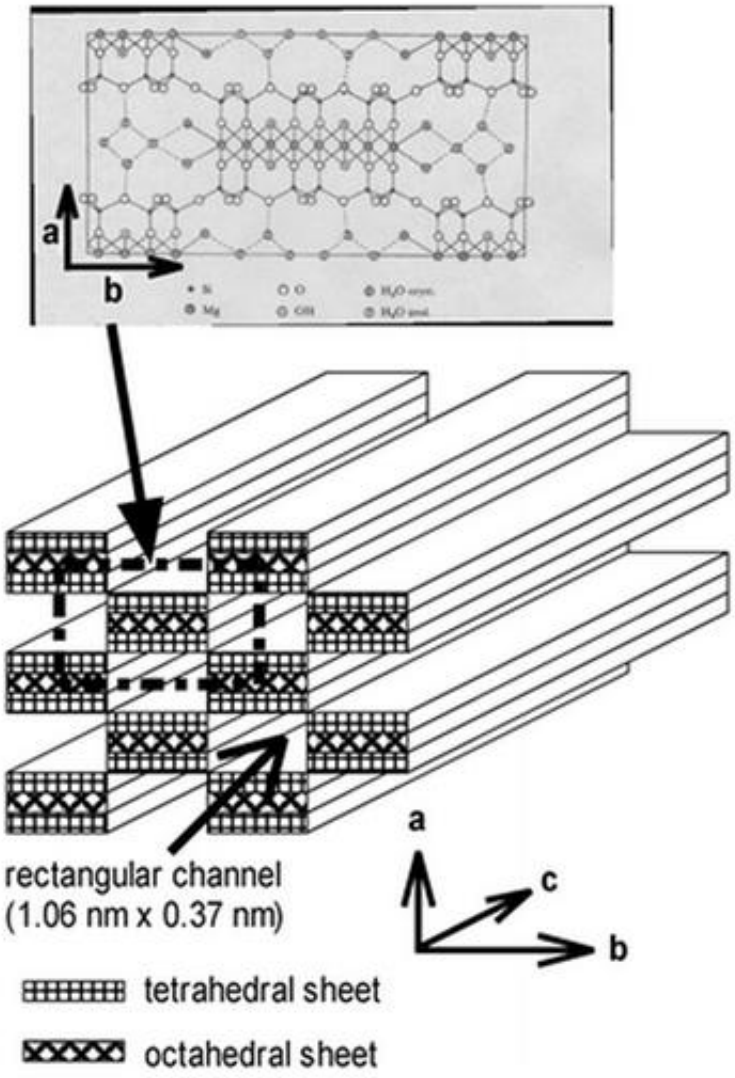


**Figure 2.29 :** Structure of sepiolite [34]

## 2.7 Literature review

In this section, literature overview about polyurethane systems and halloysite, bentonite and sepiolite minerals is stated. The use of polyurethane and clay minerals are widespread in various fields. The mechanical, thermal and chemical performances of polyurethane can be improved by changing the starting chemicals or by using some additives.

Ahmed Rehab and co-workers used sodium montmorillonite for investigating the effect of organoclay in polyurethane-nanocomposite materials via in situ polymerization. TDI, THF, Na-MMT, PEG-400, PEG-1540, DMF were the main materials for in-situ polymerization. The synthesis of polyurethane–organoclay hybrid films were carried out by swelling the organoclay [12-aminododecanoic acid montmorillonite] into different kinds of diols followed by addition of diisocyanate then casting in a film. The homogeneous dispersion of MMT in the polymer matrix is evidenced by scanning electron microscope (SEM) and X-ray diffraction (XRD), which showed the disappearance of the peak characteristic to $d_{001}$ spacing. It was found that the presence of organoclay has improved the thermal, solvent resistance and mechanical properties. Also, the tensile strength is increased with increasing the organoclay contents to 20% by the ratio 182% related to the PU with 0% organoclay. On the contrary, the elongation was decreased with increasing the organoclay contents, as expected [43].

Hongxiang Chen and his colleagues reported that sepiolite is dispersed homogeneously in the polyurethane matrix at a nanometer scale. They used sepiolite, -aminopropyl triethoxyl silane, xylene, hydroxyl-terminated polybutadiene, polyoxytetramethylene glycol and toluene diisocyanate for synthesis of polyurethane-clay nanocomposite. In this study, the sepiolite/PU composites with nanostructure were prepared. The morphology of nanocomposites and the dispersion of sepiolite were characterized by Fourier transform infrared spectroscope (FTIR), XRD, SEM, and transmission electron microscope (TEM). The mechanical properties of nanocomposites were tested by the tensile machine. The good dispersion of sepiolite in PU matrix, as well as the strong interfacial interaction between the organic and the inorganic phases, was identified by XRD, SEM, TEM and FTIR. The results for tensile strength and tensile modulus show that the

enhancement of their mechanical properties is due to the good dispersion of sepiolite in PU matrix and the strong interaction between sepiolite and the PU matrix. The thermal stability of the sepiolite/PU nanocomposites increases with the addition of sepiolite [44].

Ling Jiang and co-workers stated that reinforcement and toughening of polyurethane was made of composites with carbon nanotube/halloysite nanotube hybrids. In this work, three-dimensional (3D) hybrid nanofillers, composed of acid-treated multi-walled carbon nanotubes (a-CNTs) and silane-treated halloysite nanotubes (s-HNTs), have been successfully prepared through covalent bonding. By using simple solution-casting method, polyurethane (PU) elastomers reinforced with these s-HNT/a-CNT (HC) hybrid nanofillers have been fabricated. The morphology and mechanical properties of the resultant hybrid and PU composites are characterized by FTIR, TEM, thermogravimetric analysis (TGA) and tensile tests. Tensile test data show that the tensile strength, Young's modulus and elongation at break of the resultant PU composite with merely 1 wt% HC hybrids are significantly improved by 140%, 35% and 68% respectively. This clearly demonstrates the synergistic reinforcement of one-dimensional CNTs and HNTs within the hybrid in improving the strength and toughness of PU composite. Therefore, the s-HNT/a-CNT hybrid thus prepared is an ideal agent for simultaneous reinforcement and toughening of PU elastomers [45].

Y.W. Chen-Yang and his colleagues reported that high improvement in the properties of exfoliated PU/clay nanocomposites was achieved by the alternative swelling process. In this study, stable de-aggregated solvent-swollen organic activated clay, ALA-MMT, was obtained by modifying the montmorillonite with the swelling agent, ALA, a carboxylic acid group-containing, long-chain-alkylamine. The suspension was prepared by an efficient solvent swelling process using a home-made shaking mixer. The average size of the suspended MMT particles was reduced to about 155 nm, and the d-spacing of the clay layers was expanded from 1.4 nm to about 2.1 nm. A series of PU/ALA-MMT nanocomposites were prepared from the as-prepared solvent-swollen ALA-MMT and PU. The PU/ALA-MMT nanocomposites were confirmed by the XRD diffraction patterns, and the TEM photographs exhibited a highly exfoliated structure even with as high as 7 wt% of ALA-MMT addition, resulting in tremendous reinforcements in their thermal stability, mechanical properties, and anti-corrosion protection as well. In addition,

the reinforcements were much greater than the previously reported PU/clay nanocomposites with comparable clay loadings. This is ascribed to the proper dispersion and high exfoliation of the loaded organoclay due to the reactivity of carboxylic acid groups, the long-chain structure of the swelling agent, and the stable de-aggregated solvent-swollen organoclay suspension prepared by the effective solvent swelling process using the shaking mixer [46].

Y.I. Tien and K.H. Wei investigated that MMT effects the hydrogen bonding and mechanical properties in segmented montmorillonite/polyurethane nanocomposites of different hard segment ratios. In this work, hydrogen bonding in the hard segments of the synthesized montmorillonite/polyurethane nanocomposites of various hard segment ratios was found to decrease with the increasing amount of montmorillonite regardless of the hard segment ratios, but reached plateau values at 5 wt% montmorillonite concentration. The maximal reductions of the hydrogen bonding in the polyurethane nanocomposites ranged from 20 to 37%, depending on the hard segment ratios as compared to that in the pure polyurethane. The maximal strength and the elongation at break of the polyurethane nanocomposites increased dramatically as compared to that of pristine polyurethane, and the maximal values occurred at 1 wt% montmorillonite concentration [47].

Nihal Sarier and Emel Onder ststed that organic modification of montmorillonite with low molecular weight polyethylene glycols improved the properties of polyurethane foams. This study dealed with the preparation of organoclays by intercalating poly(ethylene glycol) molecules (PEG) between Na montmorillonite (Na-MMT) layers in a clay-water suspension system. X-ray diffraction (XRD) results of organoclays revealed that galleries of MMT were expanded after their intercalation with three different low molecular weight PEGs, including PEG600, PEG1000 and PEG1500. Thus, the distance of the interlayer spacing of MMT, d=1.38 nm, was increased to d=1.72, 1.75 and 1.69 nm, respectively, in the organoclay samples. The results of FTIR, thermogravimetric (TG) and SEM analyses supported the findings of XRD and implied that the clay mineral mainly lost its hydrophilic character and gained organophilic features. The organoclay samples also presented improved thermal stabilities. In addition, polyurethane rigid nanocomposite foams composed of 2% organoclays were synthesized, and the effects

of the organoclays on the thermal and mechanical performance of the nanocomposite foams were investigated [48].

Liu Shuguang and his co-workers investigated that the effect of organic bentonite in the polyurethane nanocomposites. Polyurethane/organic bentonite nanocomposites were prepared by monomer layer-intercalation and solution layer-intercalation methods.The results indicated that the tensile strength of nanocomposites prepared by solution layer-intercalation and monomer layer-intercalation method increased by 6.4% and 41.7% respestively,and the elongation at break increased by 4.9% and 95.7% respestively than those of pure polyurethane.The structure and properties of nanocomposites prepared by monomer intercalation method were better than those of nanocomposites prepared by solution intercalation method [49].

Eliane Ayres and her colleagues investigated that the influence of bentonite type in waterborne polyurethane nanocomposite mechanical properties. Aqueous dispersion of polyurethane ionomer (PUD), based on poly (propylene glycol) (PPG) as soft segment, isophorone diisocyanate (IPDI) as diisocyanate, dimethylol propionic acid (DMPA) as ionic center, hydrazine (HZ) as crosslinker and triethyl amine (TEA) as neutralizer, was reinforced with 1 to 5 wt % of clay to obtain nanocomposites. Substitution of Na+-montmorillonite for bentonite was made by using three types of bentonite. The tensile strength and elongation at break decreased for all nanocomposites having 5% clay in comparison to pristine polyurethane. The enhancement of mechanical properties over pristine polyurethane was achieved only by using 1% of clay. The structure of layered silicates in polyurethane was found to be maintained in some extent as evidenced from wide-angle XRD analysis. Nevertheless, the rather weak and broad diffraction peaks appearing in the curves of bentonite clays nanocomposites indicated that a nanostructure of silicate in waterborne PU system has been formed using a low cost raw material and an environmental friendly aqueous polymer precursor [50].

Ana Torro-Palau and her co-workers reported that usage of sepiolite provided the improvement of thermal and mechanical properties of polyurethane nanocomposite structures. Different amounts (5-30 wt% with respect to the polyurethane content in the adhesive) of a new filler, a partially defibrillated natural hydrated magnesium silicate (sepiolite), were added to solvent-based polyurethane (PU) adhesive formulations. The rheological, mechanical, surface and adhesion properties of the PU

adhesives obtained were measured. Increase in the amount of sepiolite added to PU adhesives led to an increase in viscosity and imparted thixotropy and pseudoplasticity to the adhesive solution. However, the addition of sepiolite produced an increase in storage and loss moduli and a decrease in the mechanical properties but did not affect the surface properties of the PU adhesive films. On the other hand, the immediate (measured 30 s after joint formation) T-peel strength of roughened or (roughened + chlorinated with 1 wt% trichloroisocyanuric acid solutions in 2-butanone) styrene-butadiene rubber/PU adhesive joints was greatly improved if the adhesive was filled with up to 10 wt% sepiolite. The T-peel strength measured 72 h after bond formation was similar for the joints prepared with PU adhesives without and with up to 10 wt% sepiolite. The joint strength decreased if the amount of sepiolite in the PU adhesive was 20-30 wt%, due to the poor mechanical properties and too high moduli of the adhesives. Some interactions between the sepiolite, the polyurethane, and/or the solvent seemed to be responsible for the improved properties of filled PU adhesives. These interactions were responsible for the increased storage and loss moduli and the displacement of Tg of the PU adhesive films to higher temperature when it contained sepiolite. Furthermore, the addition of a high amount of sepiolite changed the rheological behaviour of the PU to a solid, giving rigidity to the structure, which is responsible for the reduced adhesion in roughened rubber joints produced with polyurethanes containing 20-30 wt% sepiolite [51].

# 3. EXPERIMENTAL

## 3.1 Materials

### 3.1.1 Polyurethane prepolymer

Polyurethane prepolymer was supplied from Poliser Poylurethane by FLOKSER. Its -NCO value is 1.87. Active content of polyurethane prepolymer is 49.7%.

### 3.1.2 Halloysite

Halloysite was supplied from Eczacıbaşı Esan, Turkey. Granule/grain size is less than 45 micron. HNT were measured and the results found as; 43.3% $SiO_2$, 38.4% $Al_2O_3$, 0.7% $Fe_2O_3$, 0.1 $TiO_2$, 0.08 CaO, 0.12 MgO, 0.27 $Na_2O$ and 0.12 $K_20$.

### 3.1.3 Activated bentonite and raw bentonite

Activated bentonite and raw bentonite was supplied from DORFNER firm. Their measured chemical analysis are shown in below Table 3.1;

**Table 3.1** : Chemical analysis of bentonite.

| CONTENTS | DIN/Norm | Unit | Amount |
|---|---|---|---|
| $SiO_2$ | DIN51001 | % | 57.3 |
| $Al_2O_3$ | DIN51001 | % | 19.4 |
| $Fe_2O_3$ | DIN51001 | % | 9.05 |
| $TiO_2$ | DIN51001 | % | 1.56 |
| CaO | DIN51001 | % | 0.56 |
| $Na_2O$ | DIN51001 | % | 1.07 |
| $K_2O$ | DIN51001 | % | 1.06 |
| MgO | DIN51001 | % | 3.13 |

### 3.1.4 Sepiolite

Activated sepiolite was supplied from DORFNER firm. Product appearance is free-flowing powder. Color is light ceam. Moisture is between 9-14 % and pH is 8.7.

**Table 3.2 :** Chemical analysis of sepiolite.

| CONTENTS | Unit | Amount |
|---|---|---|
| $SiO_2$ | % | 60.5 |
| $Al_2O_3$ | % | 2.7 |
| $Fe_2O_3$ | % | 1.1 |
| CaO | % | 0.9 |
| $Na_2O$ | % | 0.3 |
| $K_2O$ | % | 0.7 |
| MgO | % | 23.6 |

### 3.1.5 Toluene

Toluene was supplied from MERCK. Its chemical formula is $C_6H_5CH_3$. Molar mass of chemical is 92.14 g/mol and boiling point= 110.6 °C. Density of toluene is 0.87 g/cm$^3$ (20°C). It is liquid form at room temperature and its grade is "ACS, ISO, Reag. Ph Eur".

### 3.1.6 Catalyst

For polyurethane, we used T9 catalyst, whose name is stannous octoate/tin octoate. It is light yellow viscous liquid. Molecular formula of the chemical substance is $C_{16}H_{30}O_4Sn$ and molar mass is 405.10 g/mol. Purity of catalyst is > 97% and specific gravity is 1.23 - 1.26 g/cm$^3$.

## 3.2 Equipment

### 3.2.1 Heater with magnetic stirrer

Trademark of stirrer is C-MAG HS 4 IKAMAG®. Its speed range is 100 - 1500 rpm and heating temperature range is 50 - 500°C. It was used for heating and mixing prepolymer, clay and catalyst mixture.

### 3.2.2 Speedy moisture tester

Trademark of moisture tester is Sartorius MA 35. It was used for specify the solid content of polyurethane nanocomposite and raw materials.

### 3.2.3 Drying oven with vacuum system and desiccator

Trademark of oven is Memmert VO. Its heating temperature range is 20 - 200°C and volume is 49 lt. Vacuum oven was used for curing clay/polyurethane nanocomposite material. Vacuum oven system is shown in Figure 3.1.

Desiccator was used for protect the produced polyurethane/clay nanocomposites from moisture and external environmental conditions. Dessicator is shown in Figure 3.2.


**Figure 3.1 :** Vacuum oven.

**Figure 3.2 :** Desiccator.

### 3.2.4 Fourier transform infrared spectroscopy (FTIR)

Trademark of FTIR is THERMO. FTIR was used for to see that any raw material remains within nanocomposite material or not. In addition, for surface morphology, the microscope part of FTIR spectrometer was used. FTIR spectrometer is shown in Figure 3.3.


**Figure 3.3 :** FTIR spectrometer.

### 3.2.5 X-ray diffraction (XRD)

XRD anaysis of polyurethane/clay nanocomposite was measured using X'Pert PRO X-ray diffractometer as shown in Figure 3.5.


**Figure 3.4 :** X-ray diffractometer

### 3.2.6 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) of polyurethane/clay composites were measured by using PERKIN ELMER TGA 4000 thermal gravimetric analyzer. TGA is shown in Figure 3.4.

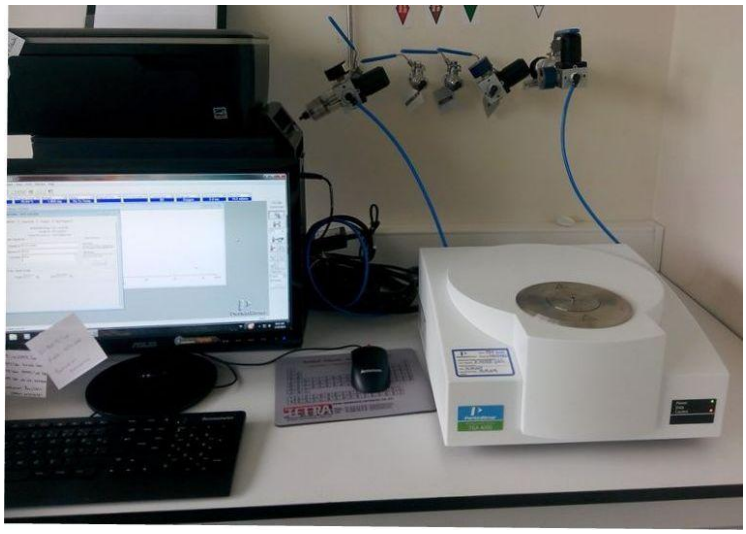

**Figure 3.5 :** Thermal gravimetric analyzer.

### 3.2.7 Mechanical test machine

Specimens tensile properties were performed by using Zwick/Roell Z0.5 universal tensile test mechine. Test machine is shown in Figure 3.6

**Figure 3.6 :** Tensile test mechine

### 3.3. Experimental Procedure

#### 3.3.1 Preparation of polyurethane/clay nanocomposite

Polyurethane prepolmer was ready to use material for this study. 4 types of set with PU were prepared. For comparison, PU samples were also synthesized without additives.

*Preparation of formulations;* Firstly, clay mineral were waited in the toluene solvent for 1 hour. Secondly, prepared solvent-clay mixture were added to polyurethane prepolymer and all mixture were heated at 80ºC degree with heater. Then, catalyst was added the PU/clay/solvent mixture and stirred 2 minutes with magnetic stirrer. Mixed solution was poured to straight template and placed in the vacuum oven at 80ºC. Samples were remained within the vacuumed oven. After 4 hour, samples were taken from oven and settled to the desiccator for 1 hour. Finally, cured samples were used for testing.

All prepared formulation details are shown in Table 3.3, Table 3.4, Table 3.5, Table 3.6 and Table 3.7.

**Table 3.3 :** Formulation of halloysite / PU study.

| CONTENTS | SET 1-1 | SET 1-2 | SET 1-3 | SET 1-4 |
|---|---|---|---|---|
| PU Prepolymer | 27 gr | 27 gr | 27 gr | 27 gr |
| Halloysite | 0.5 gr | 1.0 gr | 1.5 gr | 2.0 gr |
| Catalyst | 0.2 gr | 0.2 gr | 0.2 gr | 0.2 gr |
| Toluene | 10 gr | 10 gr | 10 gr | 10 gr |

**Table 3.4 :** Formulation of sepiolite / PU study.

| CONTENTS | SET 2-1 | SET 2-2 | SET 2-3 |
|---|---|---|---|
| PU Prepolymer | 27 gr | 27 gr | 27 gr |
| Sepiolite | 0.5 gr | 0.75 gr | 1.0 gr |
| Catalyst | 0.2 gr | 0.2 gr | 0.2 gr |
| Toluene | 10 gr | 10 gr | 10 gr |

**Table 3.5 :** Formulation of activated bentonite / PU study.

| CONTENTS | SET 3-1 | SET 3-2 | SET 3-3 |
|---|---|---|---|
| PU Prepolymer | 27 gr | 27 gr | 27 gr |
| Activated Bentonite | 0.5 gr | 0.75 gr | 1.0 gr |
| Catalyst | 0.2 gr | 0.2 gr | 0.2 gr |
| Toluene | 10 gr | 10 gr | 10 gr |

**Table 3.6 :** Formulation of raw bentonite / PU study.

| CONTENTS | SET 4-1 | SET 4-2 | SET 4-3 | SET 4-4 |
|---|---|---|---|---|
| PU Prepolymer | 27 gr | 27 gr | 27 gr | 27 gr |
| Raw Bentonite | 0.75 gr | 1.0 gr | 1.5 gr | 2.0 gr |
| Catalyst | 0.2 gr | 0.2 gr | 0.2 gr | 0.2 gr |
| Toluene | 10 gr | 10 gr | 10 gr | 10 gr |

**Table 3.7 :** Formulation of pure PU study.

| CONTENTS | SET 5-1 |
|---|---|
| PU Prepolymer | 27 gr |
| Catalyst | 0.2 gr |
| Toluene | 10 gr |

During curing of polyurethane prepolymer, all toluene and volatile content of PU prepolymer vaporized. According to these properties, percentages of PU-clay nanocomposite mixtures are given Table 3.8;

**Table 3.8 :** Percentages of PU/clay nanocomposite mixtures.

| SAMPLES | Polyurethane Prepolymer (wt %) | Halloysite (wt %) | Raw Bentonite (wt %) | Activated Bentonite (wt %) | Sepiolite (wt %) |
|---|---|---|---|---|---|
| Polyurethane Prepolymer | 100 | | | | |
| PU Prepolymer + Halloysite | 96.4 | 3.6 | | | |
| | 93 | 7.0 | | | |
| | 90 | 10 | | | |
| | 87 | 13 | | | |
| PU Prepolymer + Raw Bentonite | 94.7 | | 5.3 | | |
| | 93 | | 7.0 | | |
| | 90 | | 10 | | |
| | 87 | | 13 | | |
| PU Prepolymer + Activated Bentonite | 96.4 | | | 3.6 | |
| | 94.7 | | | 5.3 | |
| | 93 | | | 7.0 | |
| PU Prepolymer + Sepiolite | 96.4 | | | | 3.6 |
| | 94.7 | | | | 5.3 |
| | 93 | | | | 7.0 |

## 3.4 Characterization of Samples

### 3.4.1 FTIR analysis

The specimen structures were measured by means of Fourier Transform Infrared (FTIR-ATR) spectroscopy. IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Analysis of samples were applied with this method by definition of functional groups [36].

FTIR analysis was realized over the range of 500 to 4000 $cm^{-1}$ at room temperature. Samples were prepared to determine the clay components in the prepared samples.

### 3.4.2 X-ray diffraction analysis

X-ray diffraction (XRD) is an analytical technique looking at X-ray scattering from crystalline materials. Each material produces a unique X-ray "fingerprint" of X-ray intensity versus scattering angle that is characteristic of it is crystalline atomic structure. Qualitative analysis is possible by comparing the XRD pattern of an unknown material to a library of known patterns.

X-ray diffraction (XRD) patterns of the samples were recorded by monitoring the diffraction angles (2θ) from 2° to 20° on the diffractometer, using CuKα radiation. The wavelength used was λ=1.5405 Å. The XRD measurements of PU nanocomposites containing different clay (halloysite, bentonite and sepiolite) percentages (3.6 – 13 wt %) show diffraction peaks all shifted to lower 2θ degrees against the peak of pure clays and PU.

### 3.4.3 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) of the prepared PU/clay nanocomposites were carried out by using thermal gravimetric analyzer from 20ºC to 800ºC at a heating rate 10 ºC/min. Air was used as a carrier gas with a constant flow rate during analysis.

### 3.4.4 Measurement of tensile properties

The tensile test is one of the tests that measure the mechanical properties, strength of materials. The tensile test measure the design criteria: tensile strength, yield strength, Young modulus (strength), elongation at break etc. The tensile test gives a "stress-strain curve". From this curve, it is possible to calculate all the necessary mechanical properties.

Maximum tensile strength, percentage elongation at break is indicated and elastic modulus or Young modulus was calculated for all samples.

Calculated results of the standart deviations of the tensile test mesurements were also determined as between 2.5-8.5 % for maximum tensile strength, 3.5-7.5% for percent elongation and 1.3-8% for elastic modulus depending on the nanocomposite samples.

# 4. RESULTS AND DISCUSSION

## 4.1 Fourier Transform Infrared (FTIR) Analysis

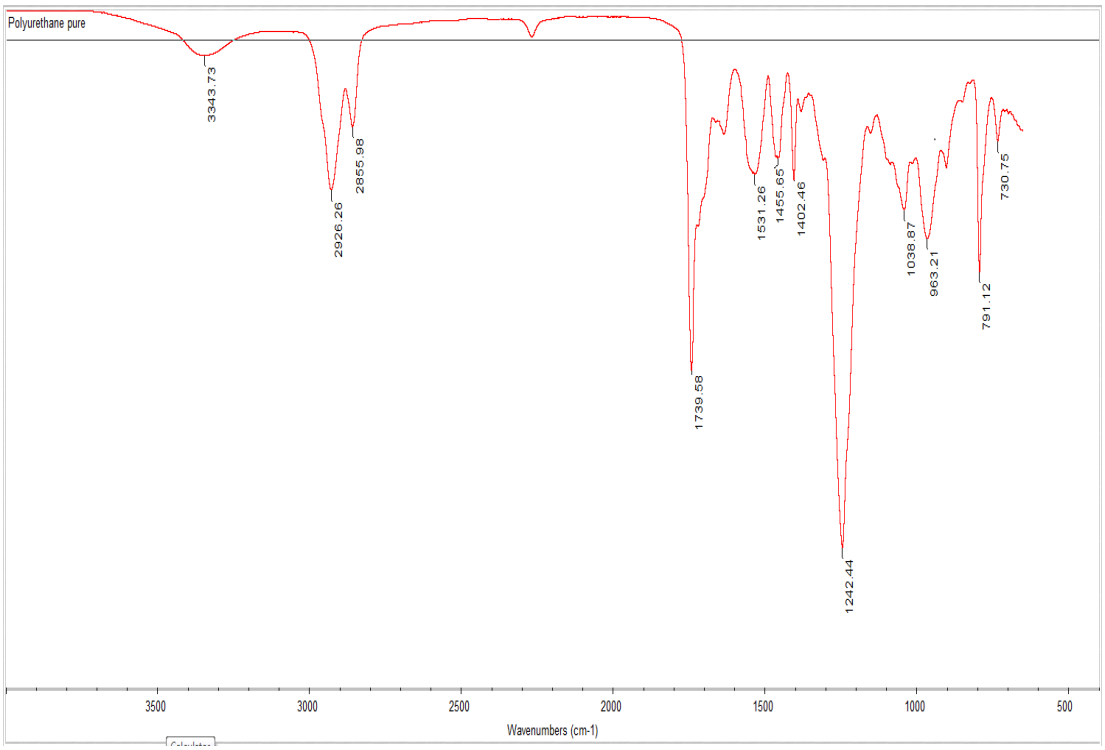


**Figure 4.1 :** Pure polyurethane FTIR analysis.

In the IR spectra of pure polyurethane are shown in Figure 4.1. Characteristic bands occurred due to the stretching vibration of Si–O at 1038 $cm^{-1}$ and Al–O at 963 $cm^{-1}$. –CH stretching vibration bands at 2855 and 2926 $cm^{-1}$ which corresponding to the hydrocarbon chains of the modifier were also occurred. The -NH stretching vibration showed characteristic peak near 3343 $cm^{-1}$. The PU indicated prominent absorption bands at 1709 $cm^{-1}$ due to stretching of -C=O (hydrogen bonded). The absorption bands occurred at 1531 $cm^{-1}$ due to stretching and deformation vibrations of the -NH group (hydrogen bound urethane).

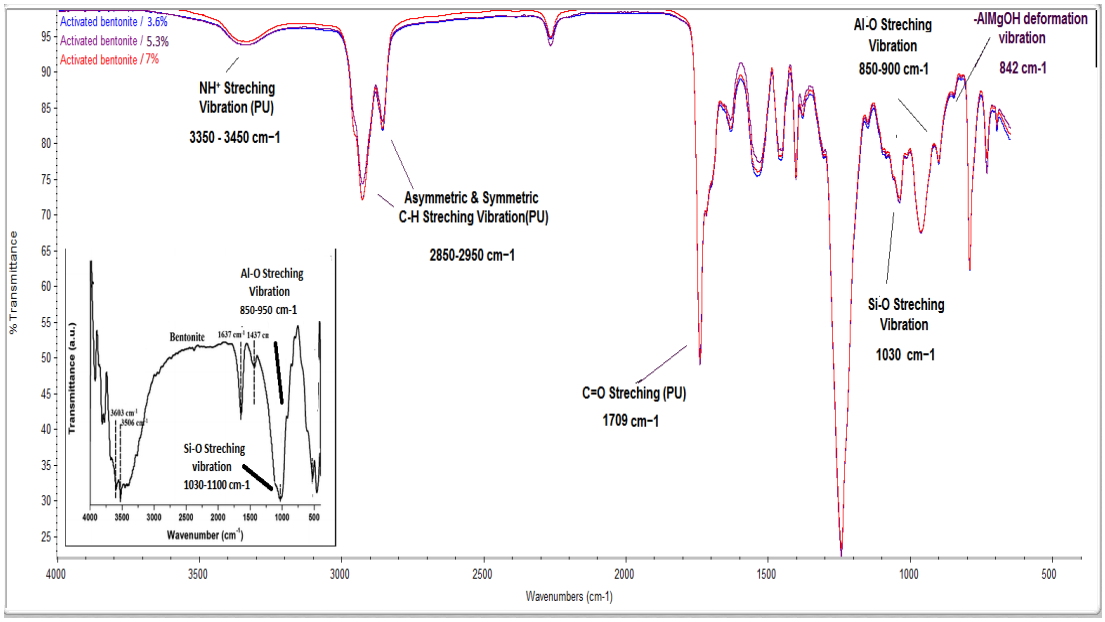


**Figure 4.2 :** Activated bentonite/PU nanocomposite FTIR analysis.

In the IR spectra of polyurethane / activated bentonite nanocomposites are shown in Figure 4.2. The clay mineral's characteristic bands occurred due to the stretching vibration of Si–O at 1030 $cm^{-1}$ and Al–O at 850-900 $cm^{-1}$. –CH stretching vibration bands at 2850 and 2950 $cm^{-1}$ which corresponding to the hydrocarbon chains of the modifier were also occurred. The $NH^{+}$ stretching vibration showed near 3350 – 3450 $cm^{-1}$. The PU indicated prominent absorption bands at 1709 $cm^{-1}$ due to stretching of C=O (hydrogen bonded). The absorption bands occurred at 1550 $cm^{-1}$ due to stretching and deformation vibrations of the -NH group (hydrogen bound urethane). The band characteristic of -NH shifted from 3343 $cm^{-1}$ to 3357 $cm^{-1}$ in the nanocomposite and the band characteristic to -C=O (1743 $cm^{-1}$) in PU was shifted to 1709 $cm^{-1}$.

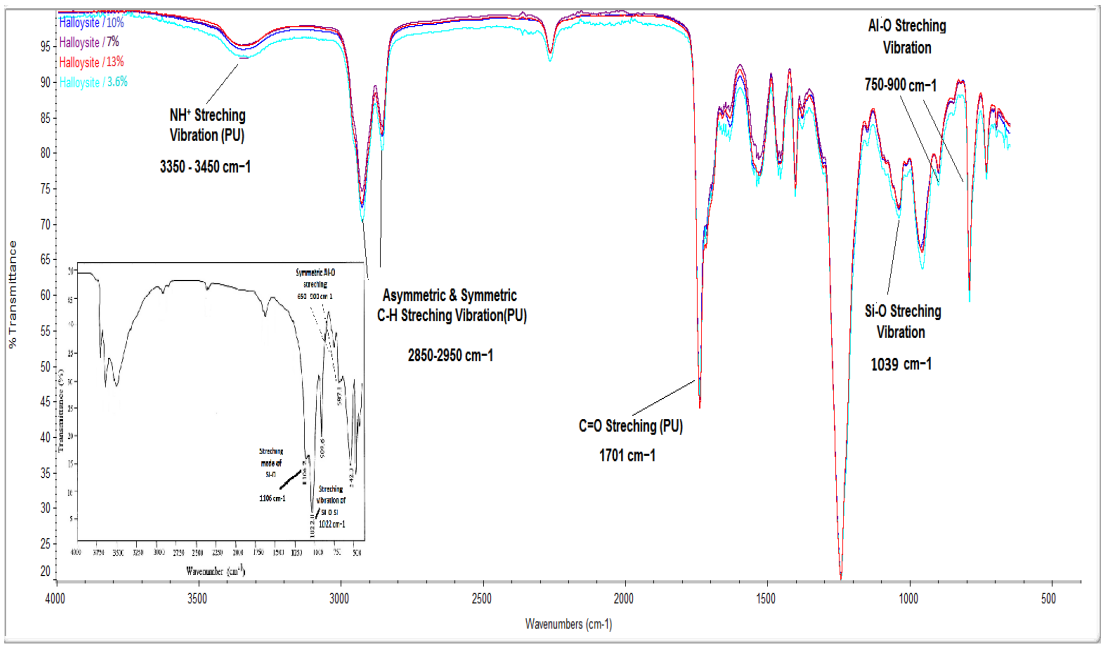


**Figure 4.3 :** Halloysite/PU nanocomposite FTIR analysis.

In the IR spectra of polyurethane/halloysite nanocomposites are shown in Figure 4.3. Characteristic bands of the clay mineral particles occured due to the stretching vibration of Si–O at 1039 $cm^{-1}$ and Al–O at 750-900 $cm^{-1}$. –CH stretching vibration bands at 2850 and 2950 $cm^{-1}$ which corresponding to the hydrocarbon chains of the modifier were also occurred. The -NH stretching vibration showed characteristic peak near 3350 – 3450 $cm^{-1}$. The PU showed prominent absorption bands at 1701 $cm^{-1}$ due to stretching of -C=O (hydrogen bonded). The absorption bands occurred at 1550 $cm^{-1}$ due to stretching and deformation vibrations of the -NH group (hydrogen bound urethane). The band characteristic to -NH shifted from 3343 $cm^{-1}$ to 3350 $cm^{-1}$ in the nanocomposites and the band characteristic to -C=O (1743 $cm^{-1}$) in PU was shifted to 1701 $cm^{-1}$.

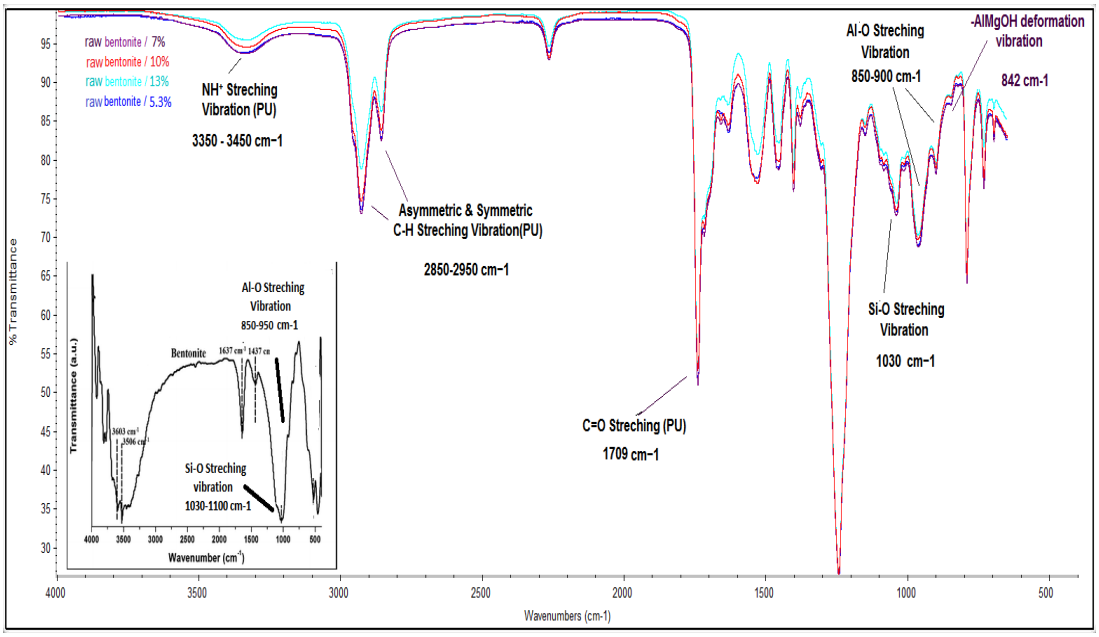


**Figure 4.4 :** Raw bentonite/PU nanocomposite FTIR analysis.

In the IR spectra of polyurethane/raw bentonite nanocomposites are shown in Figure 4.4. The clay mineral particle in produced characteristic bands occurred due to stretching vibration of Si–O at 1030 $cm^{-1}$ and Al–O at 850-900 $cm^{-1}$. –CH stretching vibration bands at 2850 and 2950 $cm^{-1}$ which corresponding to the hydrocarbon chains of the modifier were also occurred. The -NH stretching vibration showed characteristic peak near 3350 – 3450 $cm^{-1}$. The PU indicated prominent absorption bands at 1709 $cm^{-1}$ due to stretching of -C=O (hydrogen bonded). The absorption bands occurred at 1555 $cm^{-1}$ due to stretching and deformation vibrations of the -NH group (hydrogen bound urethane). The band characteristic to -NH shifted from 3343 $cm^{-1}$ to 3350 $cm^{-1}$ in the nanocomposites and the band characteristic to -C=O (1743 $cm^{-1}$) in PU was shifted to 1709 $cm^{-1}$.

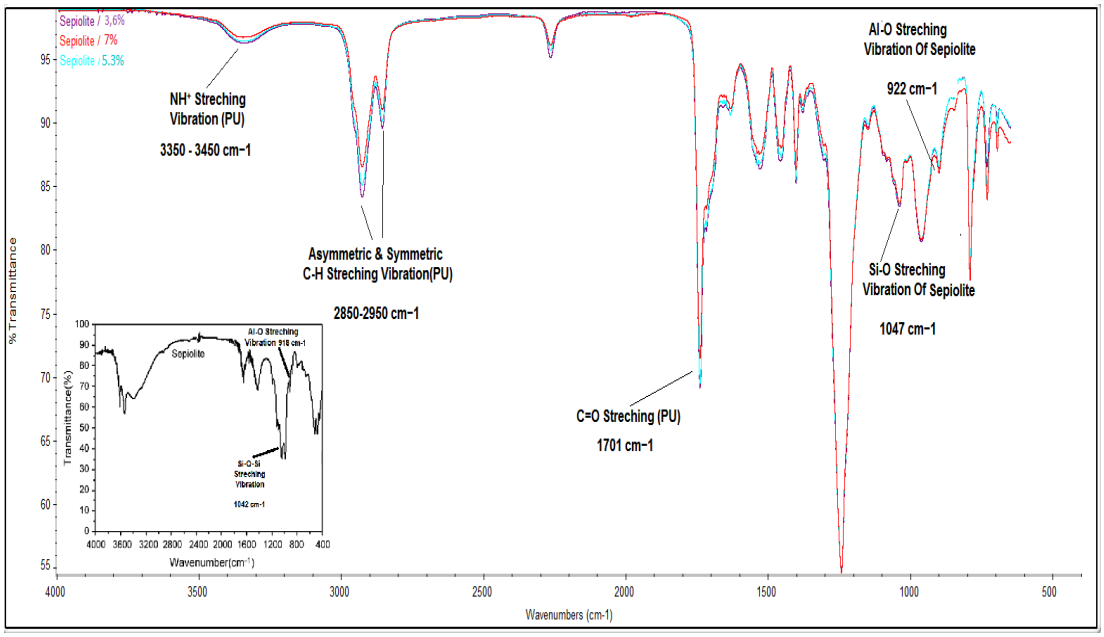


**Figure 4.5 :** Sepiolite/PU nanocomposite FTIR analysis.

In the IR spectra of polyurethane/sepiolite nanocomposites are shown in Figure 4.5. The clay mineral particle in produced characteristic bands associated with stretching vibration of Si–O (1047 $cm^{-1}$), Al–O at 922 $cm^{-1}$. –CH stretching vibration bands at 2850 and 2950 $cm^{-1}$ which corresponding to the hydrocarbon chains of the modifier were also observed. The -NH stretching vibration near 3350 – 3450 $cm^{-1}$. The PU exhibited prominent absorption bands at 1701 $cm^{-1}$ due to stretching of -C=O (hydrogen bonded). The absorption bands at 1550 $cm^{-1}$ were due to stretching and deformation vibrations of the -NH group (hydrogen bound urethane). The band characteristic to -NH shifted from 3343 $cm^{-1}$, sepiolite to 3360 $cm^{-1}$ in the nanocomposites and the band characteristic to -C=O (1743 $cm^{-1}$) in PU was shifted to 1701 $cm^{-1}$.

### 4.2 X-Ray Diffraction Analysis

XRD analysis result of pure halloysite is shown in Figure 4.6.

As it is shown in Figure 4.6, there is a characteristic diffraction peak at about 12° for 2Θ of halloysite. Figure 4.7 defines the XRD patterns of halloysite/polyurethane nanocomposites with clay loadings of 3.6%, 7.0%, 10% and 13%.

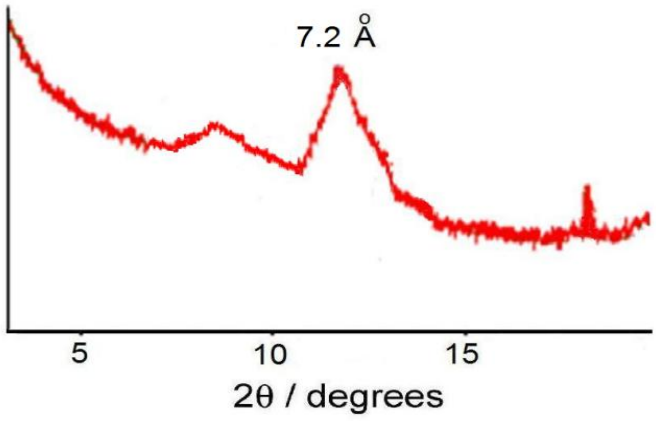


**Figure 4.6 :** XRD result of halloysite.

The same peaks obtained for clays also exist for the nanocomposites but the peak locations were nearly same. As a result, these XRD data suggest a possible increase in “layer spacing” are not observed.

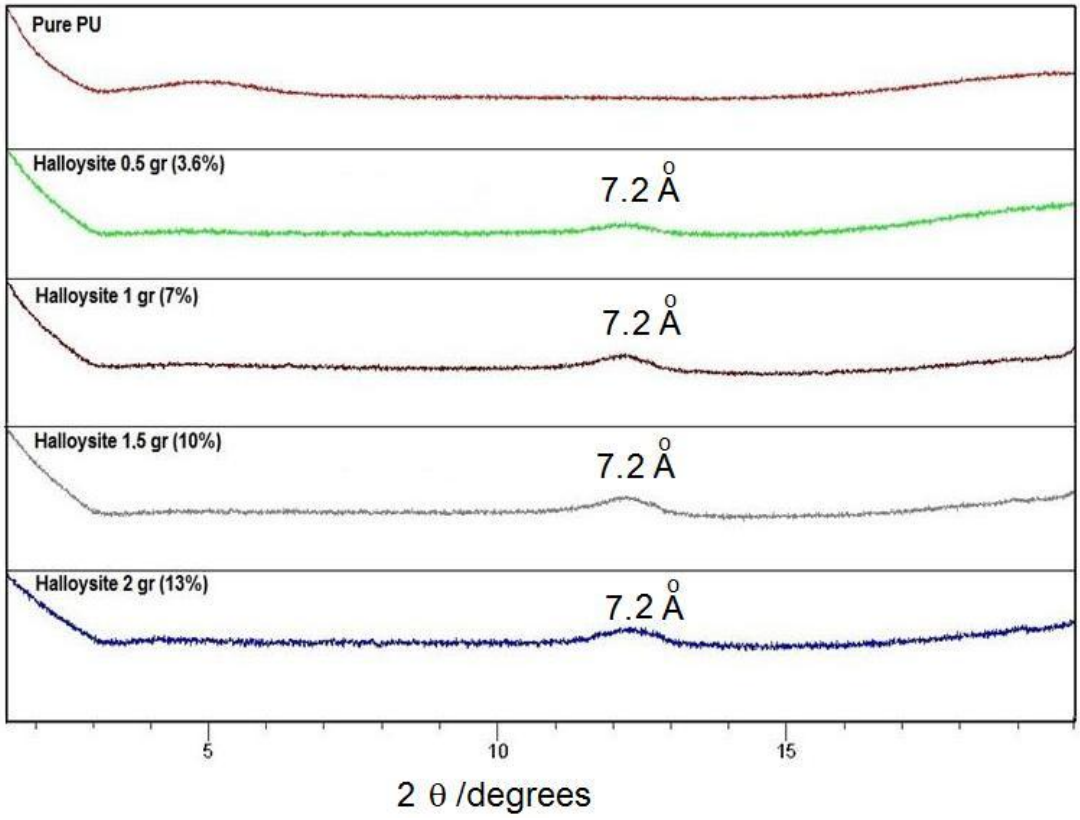


**Figure 4.7 :** XRD results of halloysite/PU nanocomposites.

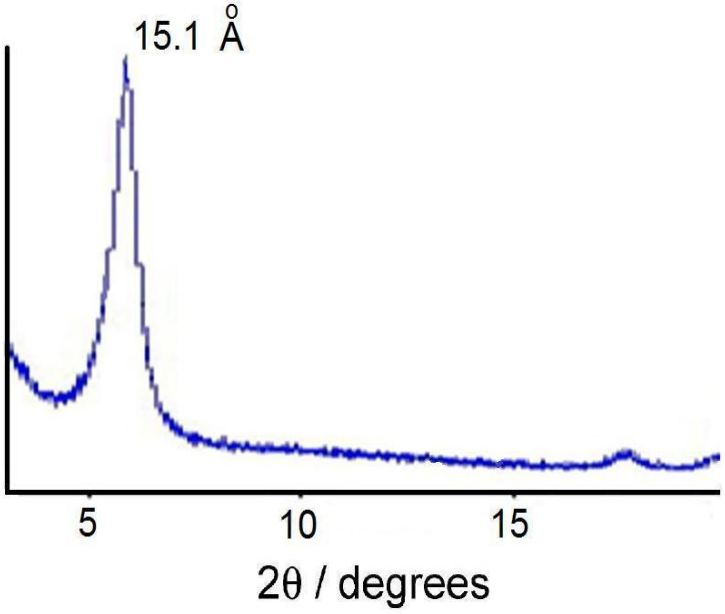


**Figure 4.8:** XRD result of bentonite.

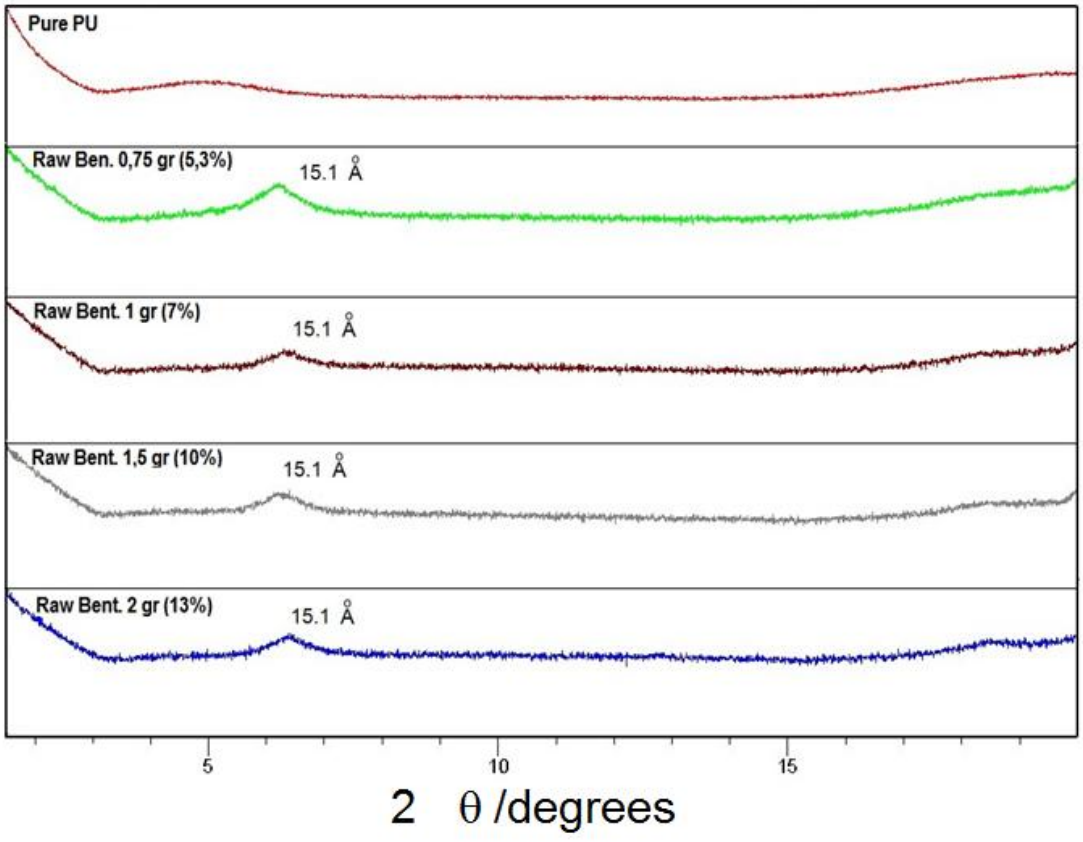


**Figure 4.9 :** XRD result of raw bentonite/PU nanocomposites.

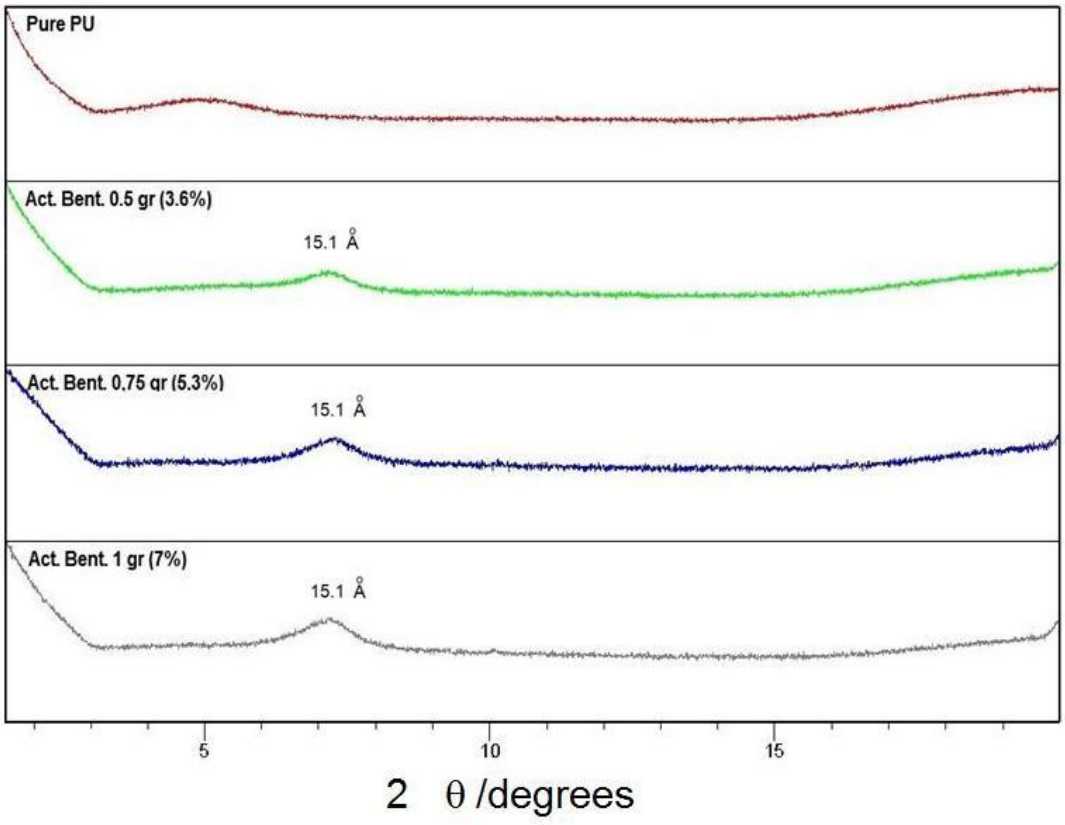


**Figure 4.10 :** XRD result of activated bentonite/PU nanocomposites

As it is seen in Figure 4.8, there is is a characteristic diffraction peak at about 6-7° for 2Θ of bentonite. Figure 4.9 shows the XRD patterns of raw bentonite/PU nanocomposites with clay loadings of 5.3%, 7.0%, 10% and 13%. Figure 4.10 shows the XRD patterns of activated bentonite/PU nanocomposites with clay loadings of 3.6%, 5.3%, 7.0%. The same peaks obtained for clays also exist for the nanocomposites but the peak locations were the same.

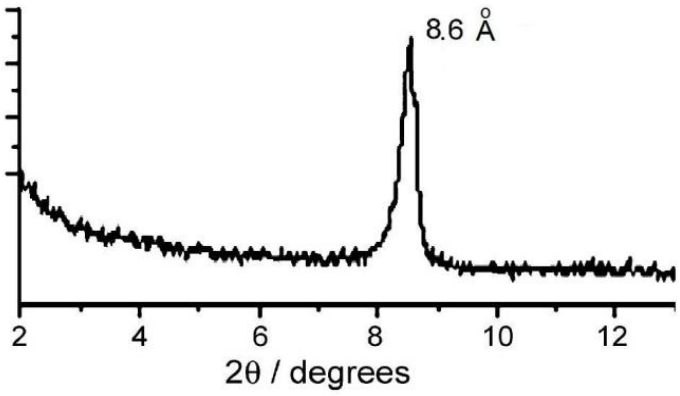


**Figure 4.11 :** XRD result of sepiolite.

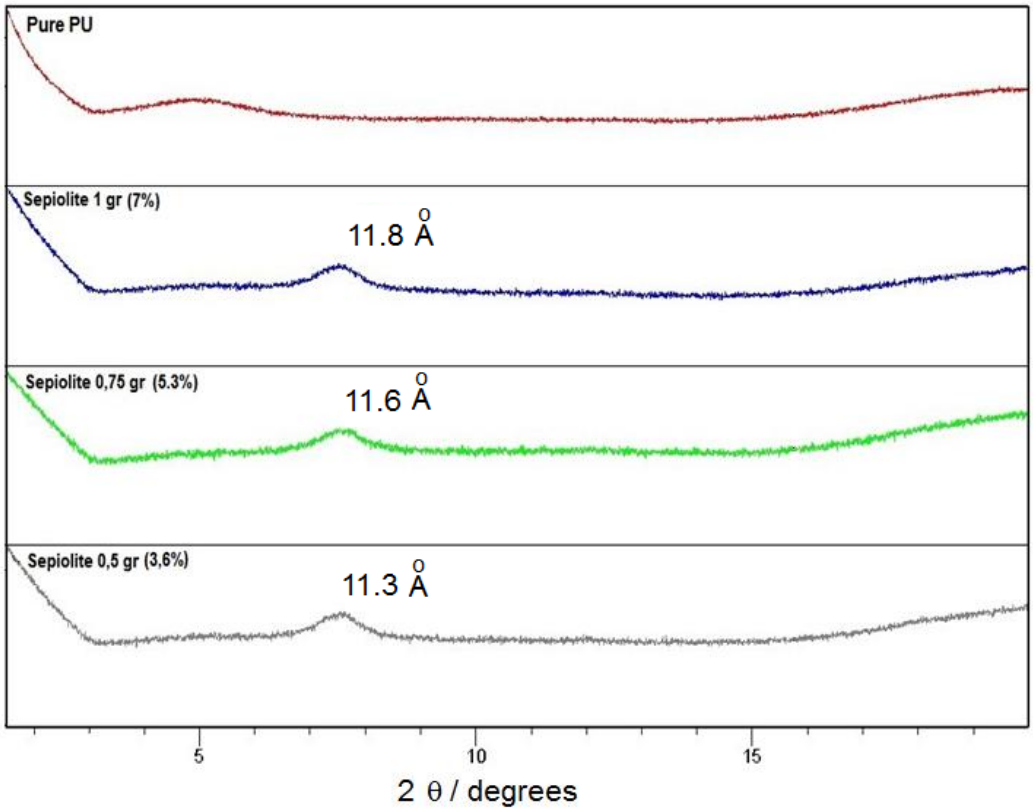


**Figure 4.12 :** XRD result of sepiolite/PU nanocomposites.

In Figure 4.11, there is is a characteristic diffraction peak at about 8.5° for 2Θ of sepiolite. Figure 4.12 shows the XRD patterns of sepiolite/PU nanocomposites with clay loadings of 3.6%, 5.3%, 7.0%.

Peak value of original sepiolite was calculated as 8.6 Å. However, for sepiolite/PU nanocomposites, this peak values were between 11.3 – 11.8 Å depending on the different loading degree. This means that, sepiolite increased layer spacing in their nanocomposites.

According to XRD results, increasing in ‘’layer spacing’’ was observed only PU/Sepiolite NC structure. Generally, it can be said that, crosslinked structures in the nanocomposites prevented to increase layer spacings.

### 4.3 Thermal Gravimetric Analysis

In the TGA analysis of polyurethane/HNT nanocomposites are shown in Figure 4.13. There were two major stages of mass loss. The first mass loss below 300°C was related to the release of free water and some volatiles. At the second stage in the temperature range at 350–600°C, intercalated clay was decomposed. The lower

molecular mass polymer was released at a lower temperature. As a result, higher halloysite percentage provided higher thermal stability for polyurethane/halloysite structure.

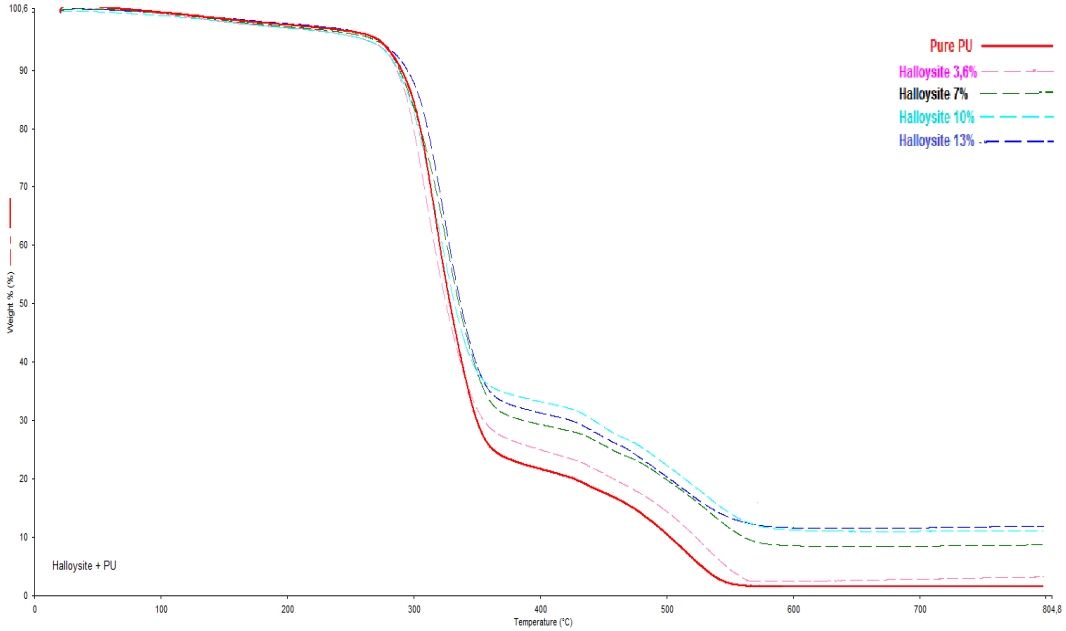


**Figure 4.13 :** TGA results of halloysite/PU nanocomposite.

Theoretical clay content, TGA residue weight, and calculated net clay residue weight percent for halloysite/PU nanocomposite are given in Table 4.1.

**Table 4.1 :** TGA results of prepared PU/HNT nanocomposites.

| Sample Name | Theoretical Clay Content (wt%) | TGA Residue Weight (wt%) | Net Clay Residue Weight (wt%) |
|---|---|---|---|
| **Pure PU** | 0 | 1.3 | 0 |
| **PU+Halloysite** | 3.6 | 4.7 | 3.4 |
| **PU+Halloysite** | 7.0 | 8.6 | 7.3 |
| **PU+Halloysite** | 10.0 | 11.2 | 9.9 |
| **PU+Halloysite** | 13.0 | 12.4 | 11.1 |

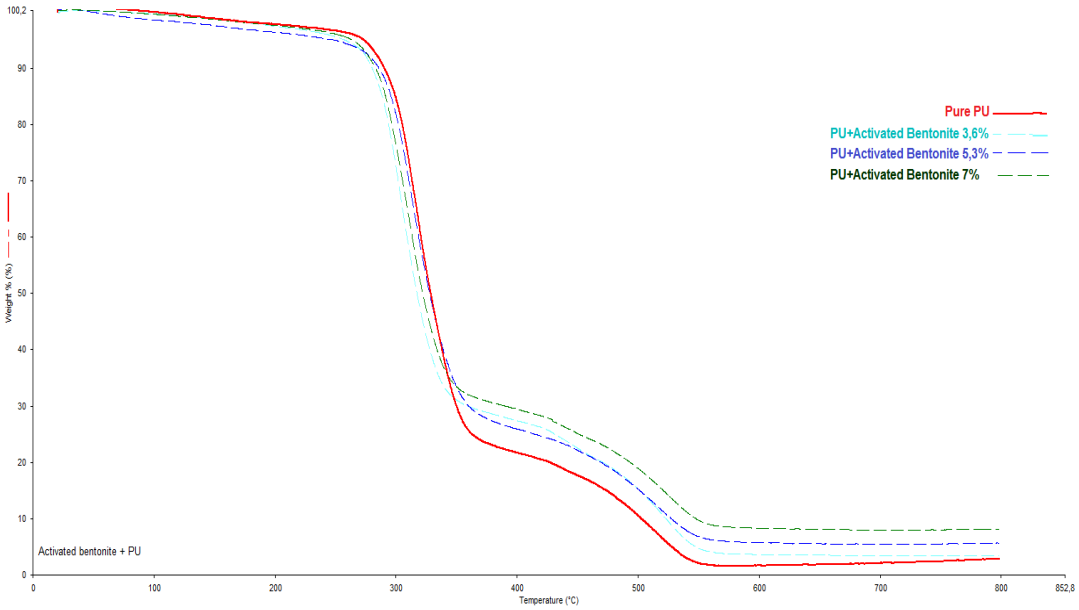


**Figure 4.14 :** TGA results of activated bentonite/PU nanocomposite.

According to the TGA results of activated bentonite/PU nanocomposite (Figure 4.14)**,** higher activated bentonite percentage provided higher thermal stability for polyurethane/activated bentonite structure.

Theoretical clay content, TGA residue weight, and calculated net clay residue weight percent for activated bentonite/PU nanocomposite are shown in Table 4.2.

**Table 4.2 :** TGA results of prepared PU/activated bentonite nanocomposites.

| Sample Name | Theoretical Clay Content (wt%) | TGA Residue Weight (wt%) | Net Clay Residue Weight (wt%) |
|---|---|---|---|
| **Pure PU** | 0 | 1.3 | 0 |
| **PU+Act. Bent.** | 3.6 | 4.7 | 3.4 |
| **PU+Act. Bent.** | 5.3 | 6.0 | 4.7 |
| **PU+Act. Bent.** | 7.0 | 8.4 | 7.1 |

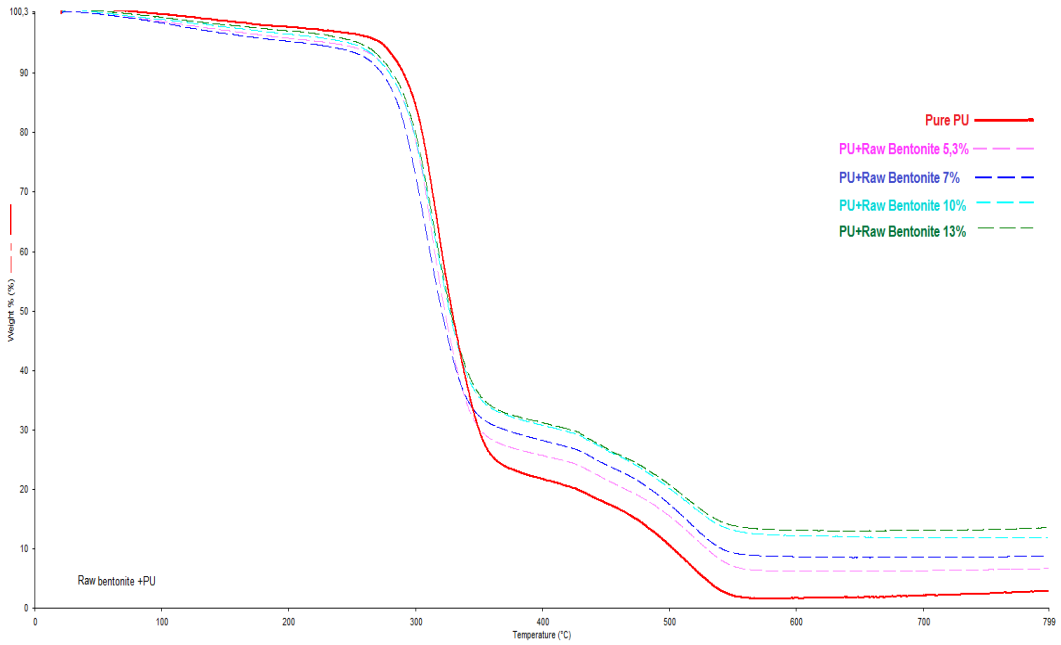


**Figure 4.15 :** TGA results of raw bentonite/PU nanocomposite.

In Figure 4.15, TGA results of raw bentonite/PU nanocomposite show that**,** higher raw bentonite percentage took about higher thermal stability for polyurethane/raw bentonite structure.

Theoretical clay content, TGA residue weight, and calculated net clay residue weight percent for raw bentonite/PU nanocomposite are shown in Table 4.2.

**Table 4.3 :** TGA results of prepared PU/raw bentonite nanocomposites.

| Sample Name | Theoretical Clay Content (wt%) | TGA Residue Weight (wt%) | Net Clay Residue Weight (wt%) |
|---|---|---|---|
| **Pure PU** | 0 | 1.3 | 0 |
| **PU+Raw Bent.** | 5.3 | 6.3 | 5 |
| **PU+Raw Bent.** | 7.0 | 8.7 | 7.4 |
| **PU+Raw Bent.** | 10.0 | 12.0 | 10.7 |
| **PU+Raw Bent.** | 13.0 | 13.6 | 12.3 |

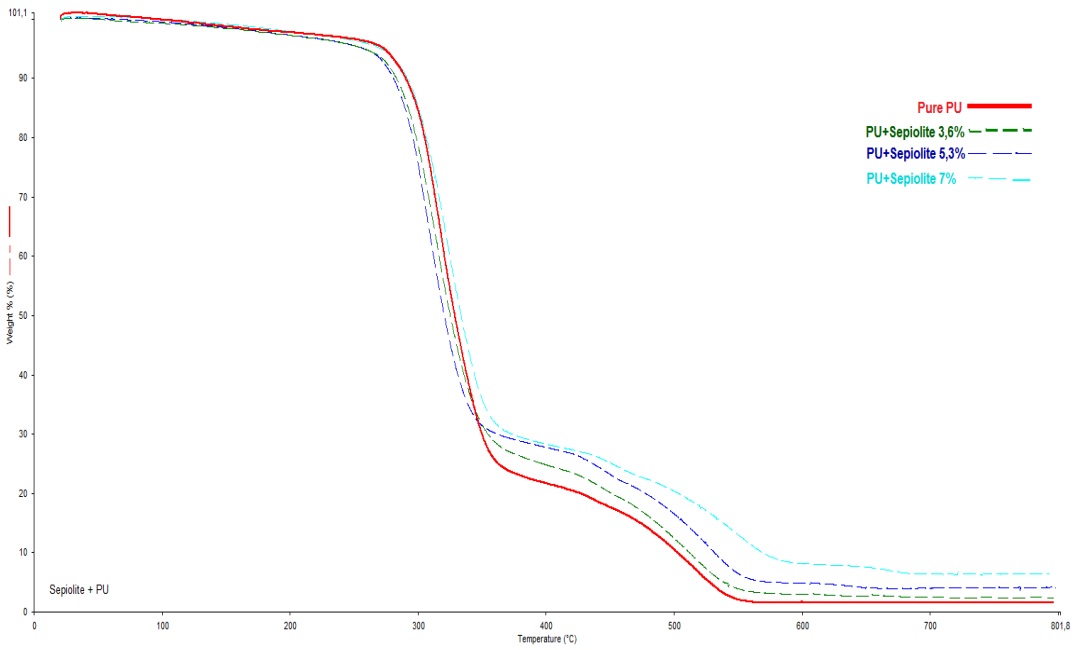


**Figure 4.16 :** TGA results of sepiolite/PU nanocomposites.

In Figure 4.16, TGA results of sepiolite/PU nanocomposite show that**,** higher sepiolite percentage provided higher thermal stability for polyurethane/sepiolite structure.

Theoretical clay content, TGA residue weight, and calculated net clay residue weight percent for raw bentonite/PU nanocomposites are shown in Table 4.4.

**Table 4.4 :** TGA results of prepared PU/sepiolite nanocomposites.

| Sample Name | Theoretical Clay Content (wt%) | TGA Residue Weight (wt%) | Net Clay Residue Weight (wt%) |
|---|---|---|---|
| **Pure PU** | 0 | 1.3 | 0 |
| **PU+Sepiolite** | 3.6 | 4.3 | 3.0 |
| **PU+Sepiolite** | 5.3 | 6.4 | 5.1 |
| **PU+Sepiolite** | 7.0 | 8.1 | 6.8 |

As a result, all TGA results indicated that, halloysite, sepiolite, raw&activated bentonite type clays shifted the decomposition temperature of polyurethane. Nano additives increased the thermal stability of polyurethane polymer structure.

If we compare the clay types in its own right; in constant residue mass (20%) and constant clay percentage (7.0%), sepiolite ensured the most favour results, it postponed the temperature from 425°C to 525°C.

**Table 4.5 :** Comparison of constant residue and temperature for halloysite.

| Halloysite (%) | Temperature in 20% residue mass |
|---|---|
| 3.6 | 490 °C |
| **7.0** | **515 °C** |
| 10 | 520 °C |
| 13 | 530 °C |

**Table 4.6 :** Comparison of constant residue and temperature for raw bentonite.

| Raw Bentonite (%) | Temperature in 20% residue mass |
|---|---|
| 5.3 | 475 °C |
| **7.0** | **495 °C** |
| 10 | 510 °C |
| 13 | 520 °C |

**Table 4.7 :** Comparison of constant residue and temperature for activated bentonite.

| Activated Bentonite (%) | Temperature in 20% residue mass |
|---|---|
| 3.6 | 475 °C |
| 5.3 | 475 °C |
| **7.0** | **500 °C** |

**Table 4.8 :** Comparison of constant residue and temperature for sepiolite.

| Sepiolite (%) | Temperature in 20% residue mass |
|---|---|
| 3.6 | 475 °C |
| 5.3 | 490 °C |
| **7.0** | **525 °C** |

**Table 4.9 :** Comparison of constant residue and temperature for pure PU.

| Halloysite (%) | Temperature in 20% residue mass |
|---|---|
| Pure polyurethane | **450 °C** |

### 4.4 Mechanical Analysis

Mechanical properties of polyurethane and its nanocomposites were determined by using mechanical testing method.

Tensile tests were done according to the procedure explained in section 3.4.4. Experimental mechanical test results of all samples are shown in Table 4.10.

**Table 4.10 :** Mechanical test results of PU and its nanocomposites.

| Samples | Loading levels (%) | Max. Tensile Strength (MPa) | Elongation (%) | Modulus (MPa) |
|---|---|---|---|---|
| Pure PU | 0 | 5.6 | 287 | 5.4 |
| PU + Halloysite | 3.6 | 8.5 | 562 | 7.2 |
| | 7.0 | 9.0 | 618 | 7.6 |
| | 10 | 9.4 | 624 | 8.9 |
| | 13 | 10 | 649 | 9.2 |
| PU + Raw Bentonite | 5.3 | 4.6 | 132 | 6.6 |
| | 7.0 | 5.3 | 285 | 7.4 |
| | 10 | 4.3 | 205 | 10.4 |
| | 13 | 4.2 | 152 | 12.6 |
| PU + Activated Bentonite | 3.6 | 5.3 | 286 | 5.5 |
| | 5.3 | 11.5 | 653 | 5.8 |
| | 7.0 | 7.1 | 516 | 5.7 |
| PU + Sepiolite | 3.6 | 11.4 | 669 | 5.0 |
| | 5.3 | 10.2 | 553 | 5.5 |
| | 7.0 | 10.1 | 546 | 5.7 |

Tensile tests were carried out for understanding influence of varying proportions of clays at different loading levels on the mechanical properties of PU nanocomposites. Modulus, tensile strength and elongation are known as the most important mechanical properties of PU nanocomposites.

#### 4.4.1 Halloysite/PU nanocomposite results

Existence of halloysite increased the tensile strength, percent elongation and elastic modulus values of polyurethane nanocomposite samples.

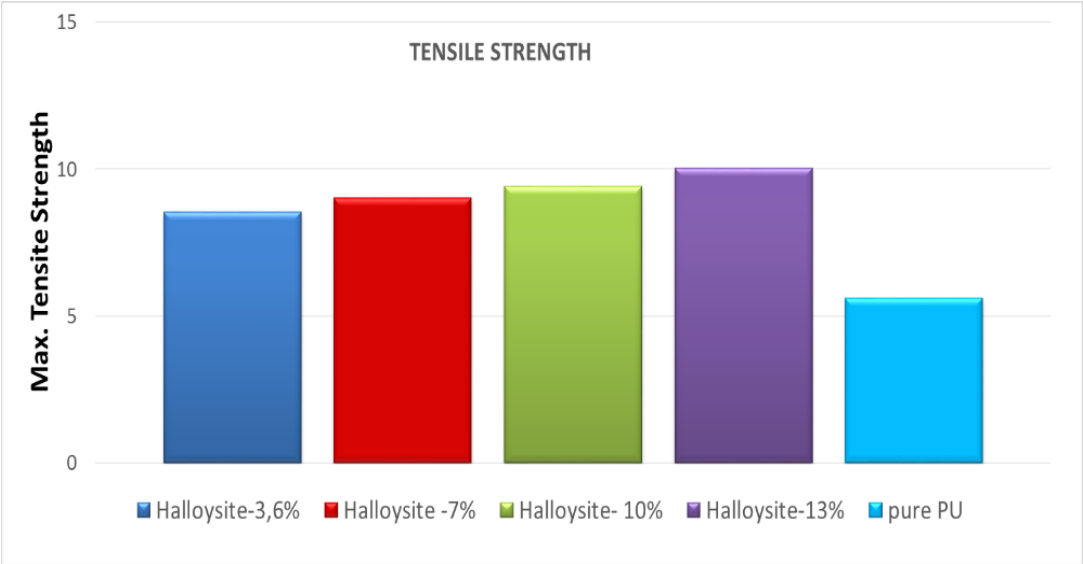


**Figure 4.17 :** Tensile strength results of PU/halloysite nanocomposites.

Tensile strength increased with increasing amounts of halloysite in PU nanocomposite structure. Tensile strength of pure PU was 5.6 MPa and the highest loading of 13.0 wt % halloysite increased the tensile strength to 10 MPa.

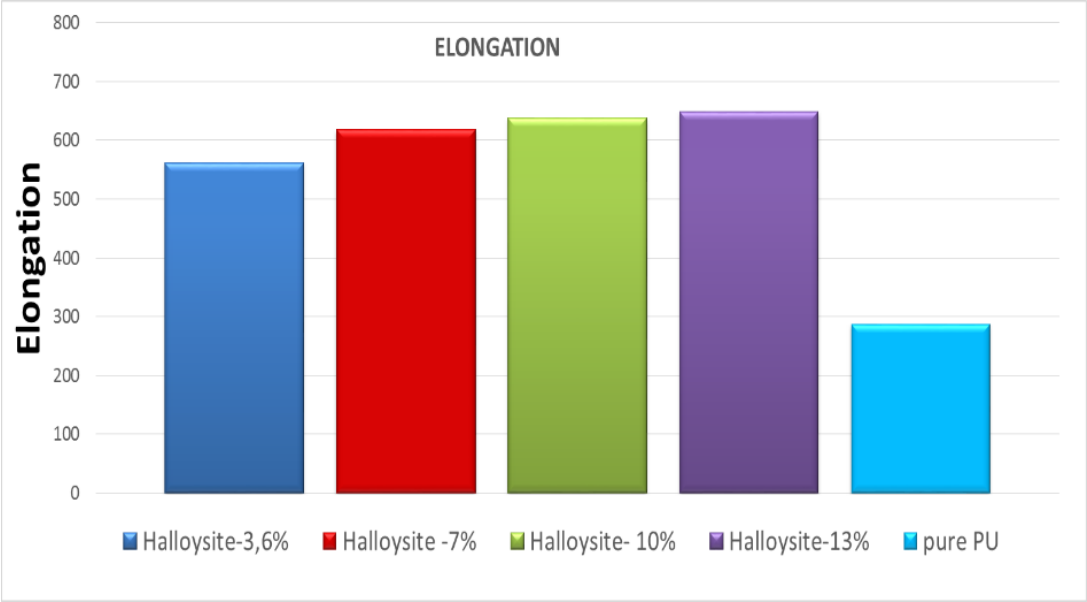


**Figure 4.18 :** Elongation results of PU/halloysite nanocomposites.

Elongation increased with increasing amounts of halloysite in PU nanocomposite. Elongation of pure PU was 287% and the highest loading of 13.0 wt % halloysite increased the elongation up to 649%.

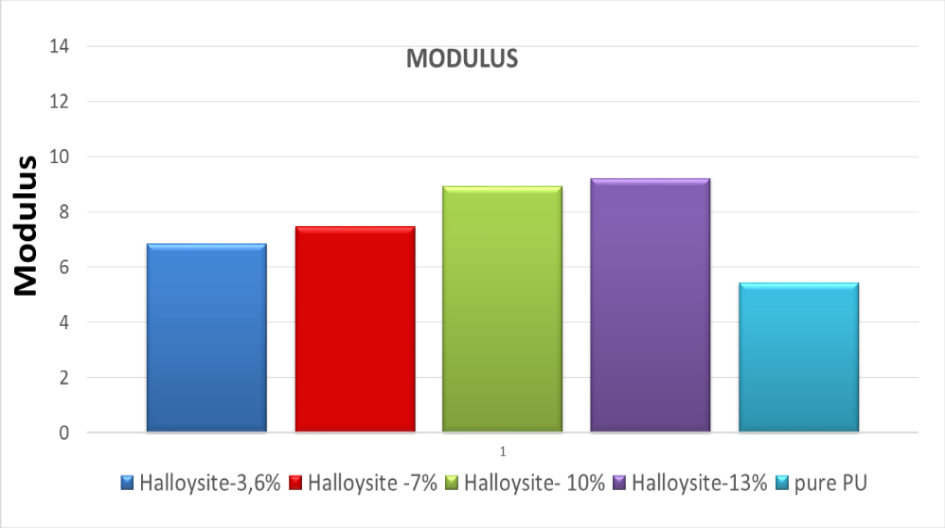


**Figure 4.19 :** Elastic modulus results of PU/halloysite nanocomposites.

Elastic modulus increased with increasing amounts of halloysite in PU nanocomposite. Elastic modulus of pure PU was 5.4 MPa and the highest loading of 13.0 wt % halloysite increased the modulus of PU/halloysite nanocomposites up to 9.2 MPa.

### 4.4.2 Raw bentonite/PU nanocomposite results

Adding raw bentonite to PU did not change the tensile strength and elongation values, but elastic modulus of polyurethane increased.

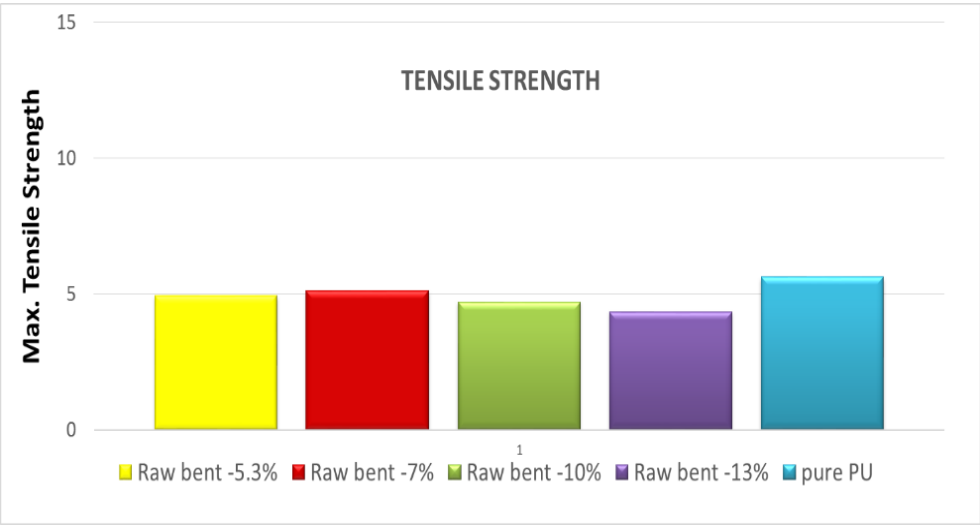


**Figure 4.20 :** Tensile strength results of PU/raw bentonite nanocomposites.

The tensile strength of pure PU was around 5.6 MPa and this was higher than loading levels of 5.3, 7.0, 10.0, 13.0% by weight of raw bentonite filled PU. Tensile (Max.) strenght properties of nanocomposites did not change with varying proportions of raw bentonite and were close to each other at the same loading levels. There were no significant differences observed.

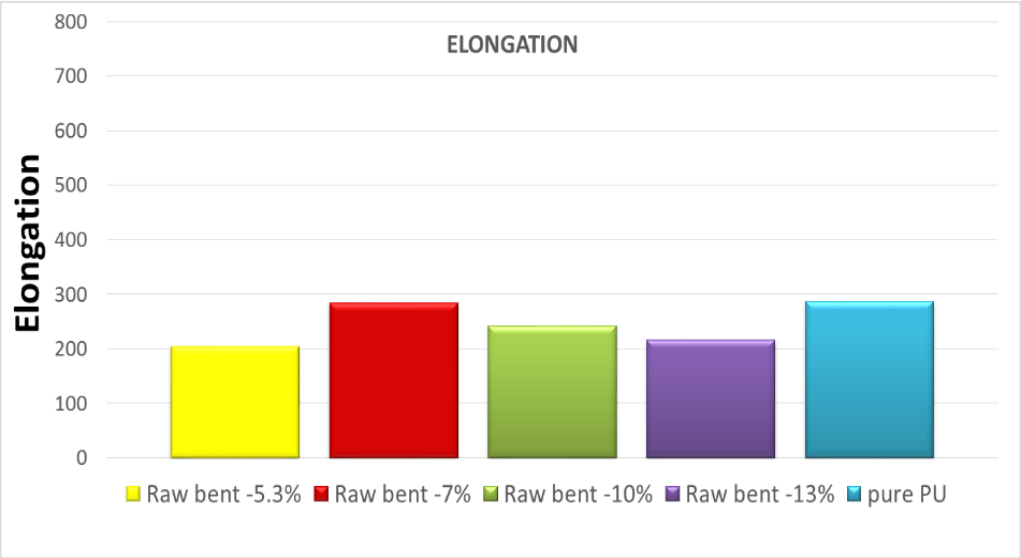


**Figure 4.21 :** Elongation results of PU/raw bentonite nanocomposites.

The elongation of pure PU was around 287 % and this was higher than loading levels of 5.3, 7.0, 10.0, 13.0% by weight of raw bentonite filled PU. Elongation properties of nanocomposites did not change with varying proportions of raw bentonite and were close to each other.

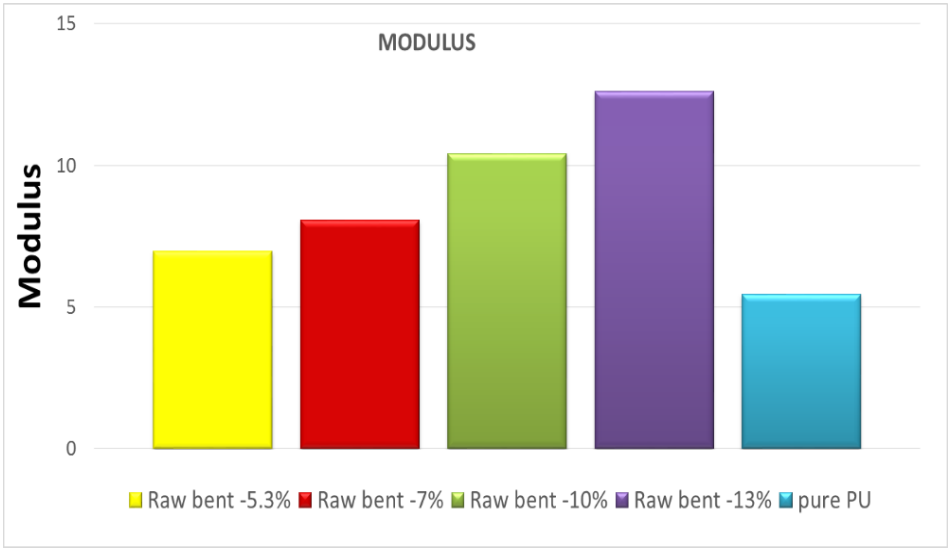


**Figure 4.22 :** Elastic modulus results of PU/raw bentonite nanocomposites.

Elastic modulus increased with increasing amounts of raw bentonite in PU nanocomposite. Elastic modulus of pure PU was 5.4 MPa and the highest loading of 13.0 wt.% raw bentonite increased the modulus up to 12.6 MPa.

### 4.4.3 Activated bentonite/PU nanocomposite results

Activated bentonite increased the tensile strength and elongation values, but elastic modulus of polyurethane remained stable.

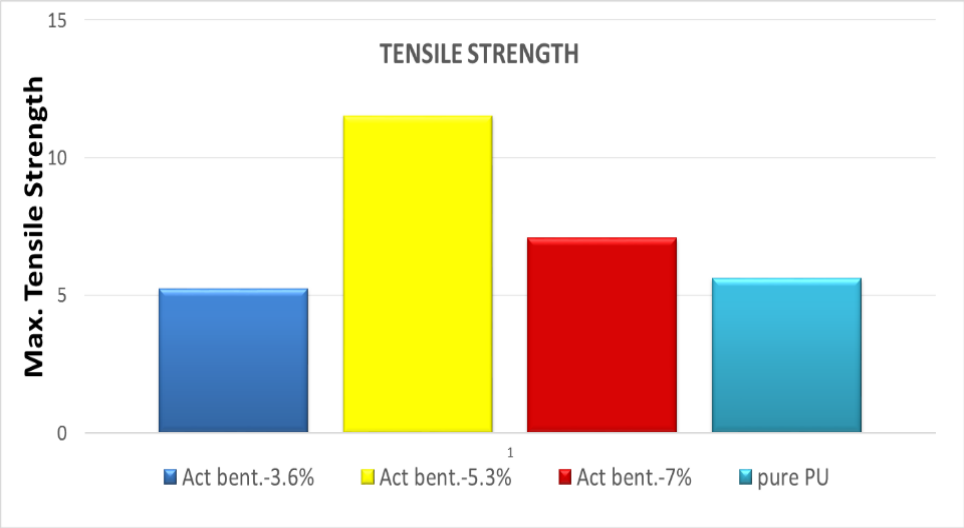


**Figure 4.23 :** Tensile strength results of PU/activated bentonite nanocomposites.

Tensile strength increased with increasing amounts of activated bentonite in PU nanocomposite structure. Tensile strength of pure PU was 5.6 MPa and the loading of 7.0 wt % activated bentonite increased the tensile strength up to 11.5 MPa.

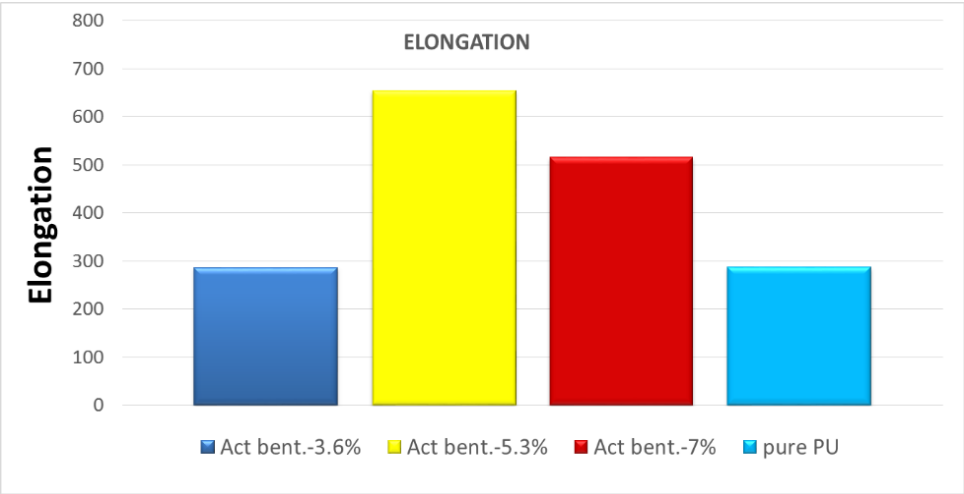


**Figure 4.24 :** Elongation results of PU/activated bentonite nanocomposites.

Elongation increased with increasing amounts of activated bentonite in PU nanocomposite. Elongation of pure PU was 287 % and the activated bentonite loading increases percent elongation increases nearly twice.

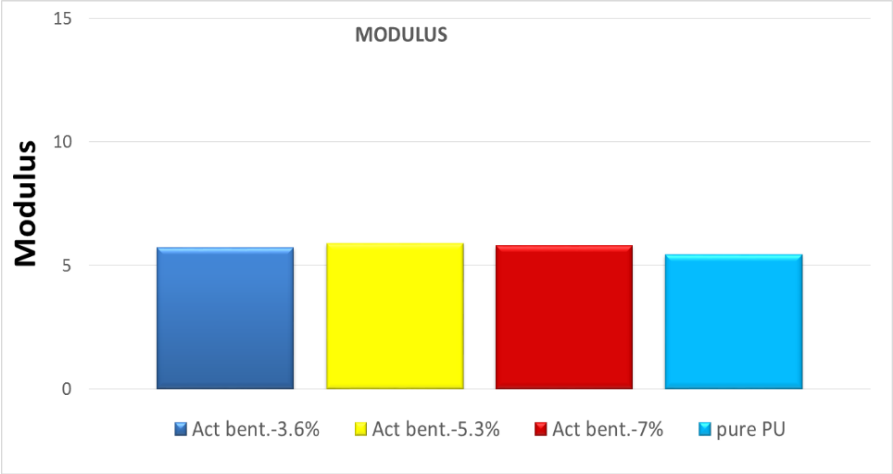


**Figure 4.25 :** Elastic modulus results of PU/activated bentonite nanocomposites.

The elastic modulus of pure PU was around 5.4 MPa and this was nearly same with loading levels of 3.6, 5.3, 7.0 % by weight of activated bentonite filled PU. Elastic modulus properties of nanocomposites did not change with varying proportions of activated bentonite and were close to each other.

### 4.4.4 Sepiolite/PU nanocomposite results

Adding sepiolite to PU increased the tensile strength, elongation values. However, increased amount of sepiolite caused reduction of the tensile strength and elongation values slightly, elastic modulus of polyurethane remained stable.

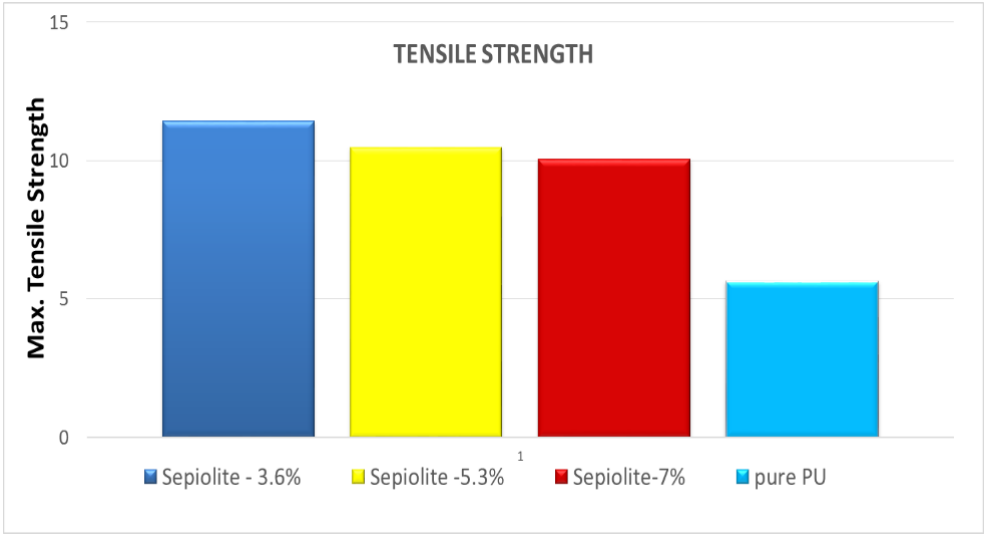


**Figure 4.26 :** Tensile strength results of PU/sepiolite nanocomposites.

Tensile strength increased with sepiolite in PU nanocomposite structure.Tensile strength of pure PU was 5.6 MPa and loading of 3.6 wt % sepiolite increased the tensile strength up to 11.5 MPa. However, increasing amount of sepiolite decreased the tensile strength, loading of 7.0 wt % sepiolite decreased the tensile strength to 10.1 MPa.

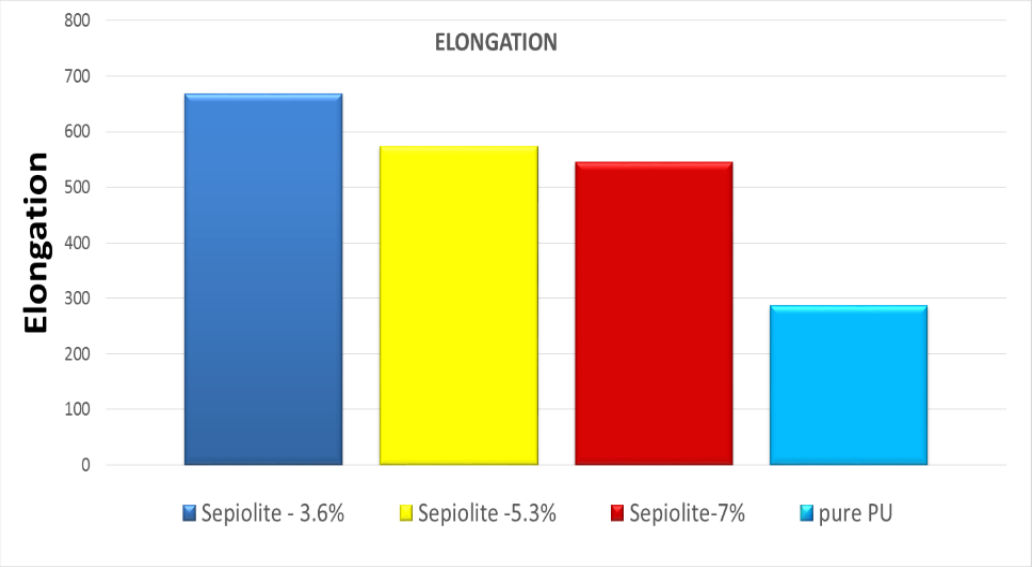


**Figure 4.27 :** Elongation results of PU/sepiolite nanocomposites.

Elongation increased with sepiolite in PU nanocomposite structure. Elongation value of pure PU was 287 % and loading of 3.6 wt.% sepiolite increased the elongation up to 669 %. However, increasing amount of sepiolite decreased the elongation value, loading of 7.0 wt.% sepiolite decreased this value to 546 %.

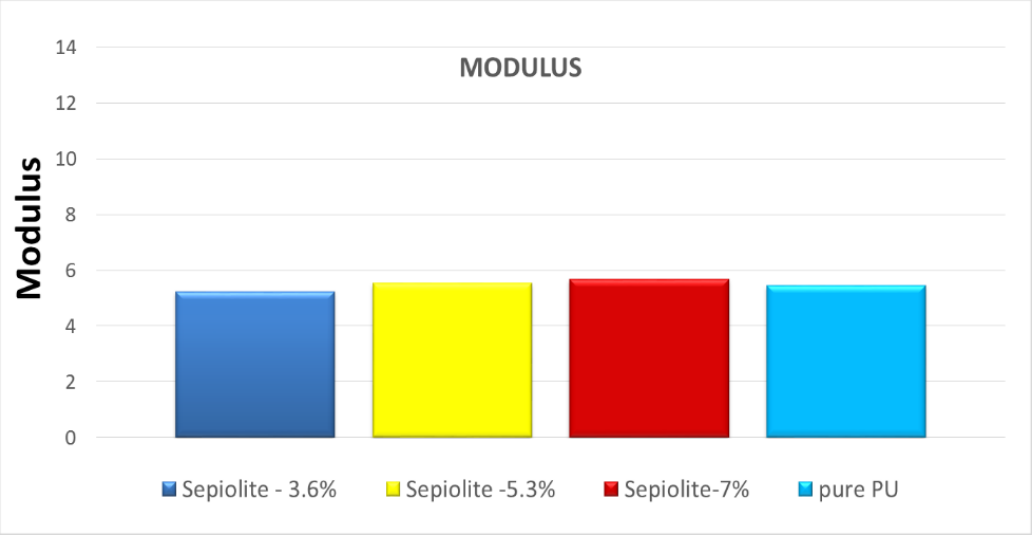


**Figure 4.28 :** Elastic modulus results of PU/sepiolite nanocomposites.

The elastic modulus of pure PU was around 5.4 MPa and this was nearly same with loading levels of 3.6, 5.3, 7.0 % by weight of sepiolite added PU. Elastic modulus properties of nanocomposites did not change with varying proportions of sepiolite and were near to each other.

## 5. CONCLUSIONS

The objective of this thesis was to investigate the physical and mechanical properties of polyurethane nanocomposites prepared using the different types of nano additives, such as halloysite, sepiolite and bentonite. The foundation of study was based on adding the different percentages of clay into the polyurethane prepolymer and then providing the curing in the presence of catalyst.

Starting of the procedure of this study, clay mineral were swelled in the toluene for 1 hour. Then, prepared solvent-clay mixture were added to polyurethane prepolymer and all mixture were heated at 80ºC degree with heater. After that, catalyst was added the PU/clay/solvent mixture and stirred 2 minutes with magnetic stirrer. Mixed solution was poured to the flat mould and placed in the vacuum oven at 80ºC. After 4 hours, samples were taken from oven and settled to desiccator for 1 hour. Finally, cured 15 samples were prepared and used for testing structurally, thermally, and mechanically.

Samples were analyzed by FTIR spectrometer between 500 and 4000 $cm^{-1}$. Pure and simple cured polyurethane sample showed all characteristic polyurethane peaks and these specific peaks of polyurethane were observed in all polyurethane nanocomposite samples.

Aim of the XRD analysis was to observe the degree of "layer spacing" of clays after curing of the nanocomposites. Analysis results showed that the distribution of the layers were successfull in sepiolite/polyurethane nanocomposite structure, especially. Distribution of clay layers in nanocomposite structures of halloysite/PU, activated bentonite/PU and raw bentonite/PU were not seen at all. Crosslinking during formation of nanocomposite structure can be prevented the complete distribution in halloysite and bentonite additives. Although, this situation did not affect the thermal and mechanical improvements of the properties of PUNC.

TGA analysis was done between 0-800ºC. According to TGA analysis of all types of clay/PUNC, it was understood that clay minerals had positive effect on the decomposition temperature of a polymeric polyurethane nanocomposites. Increasing amounts of halloysite, sepiolite, raw bentonite and activated bentonite additives also increased the decomposition temperature of polymeric polyurethane, and also each of the clay structure compared with each other. Added fixed rate of 7.0 % halloysite, sepiolite, raw and activated bentonite into the polymeric polyurethane examined. For 20 % residue mass, the halloysite shifted the pure polyurethane polymer decomposition temperature from 450ºC to 515ºC (15%), sepiolite shifted this temperature to 525ºC (17%), raw bentonite shifted temperature to 495 ºC (10%), and finally activated bentonite shifted the temperature to 500ºC (11%). The results showed that the study of sepiolite and halloysite had better performance than other types of clays.

According to the results of mechanical tests, increased halloysite amount within the polymeric polyurethane structure increased maximum tensile strength, elongation at break and elastic modulus values together. This is not a common case. Addition sepiolite into the PU structure increased the maximum tensile strength and elongation at break values. Sepiolite additive did not affect the elastic modulus of the polymeric structure. Raw bentonite addition increased the elastic modulus and tensile strength of polymeric polyurethane, but it did not affect the amount of percent elongation at break. Activated bentonite addition increased the elongation at break and maximum tensile strength of polyurethane nanocomposites, but did not affect the amount of elastic modulus.

Considering overall results, we observed inorganic clay addition to the polymeric polyurethane structures effected thermal and mechanical properties of PU structure positively.

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# APPENDICES

## APPENDIX A: Analysis Results

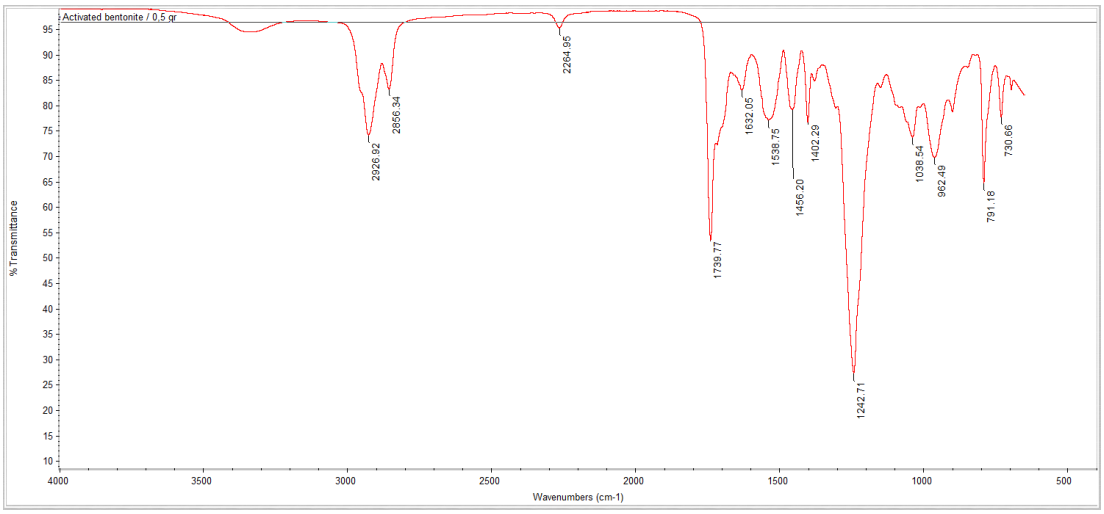


**Figure A.1 :** FTIR analysis of 3.6% activated bentonite/PU NC.

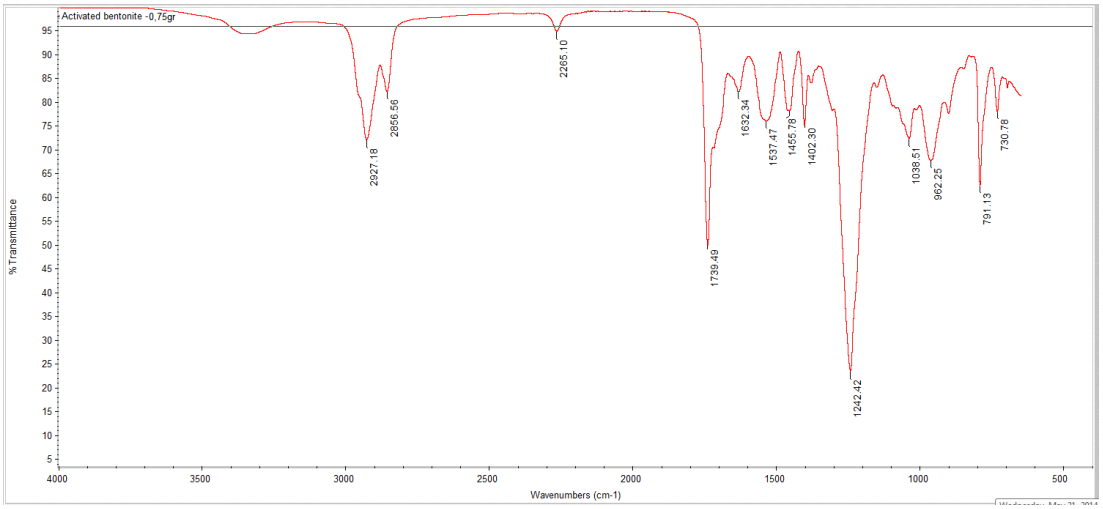


**Figure A.2 :** FTIR analysis of 5.3% activated bentonite/PU NC.

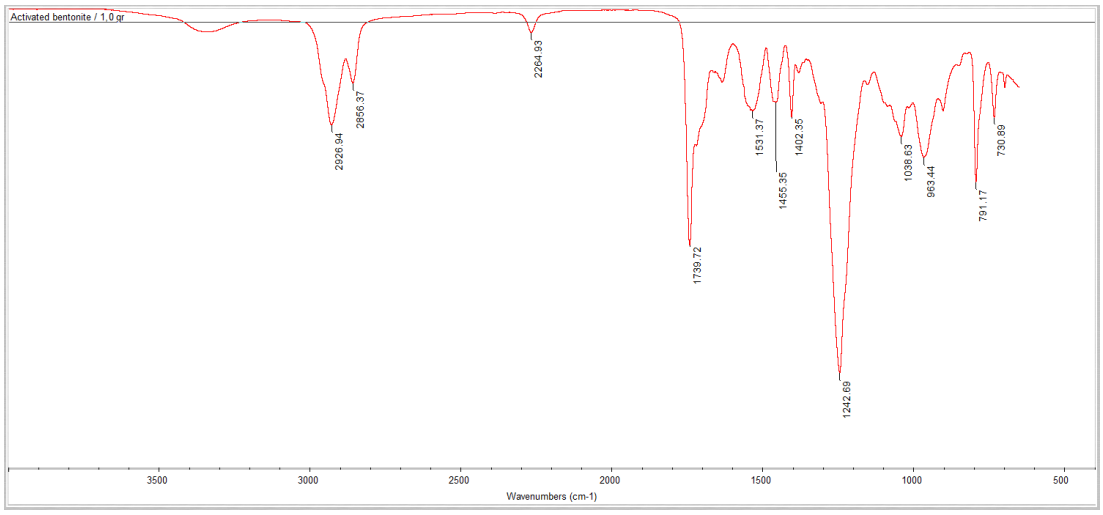


**Figure A.3 :** FTIR analysis of 7.0% activated bentonite/PU NC.

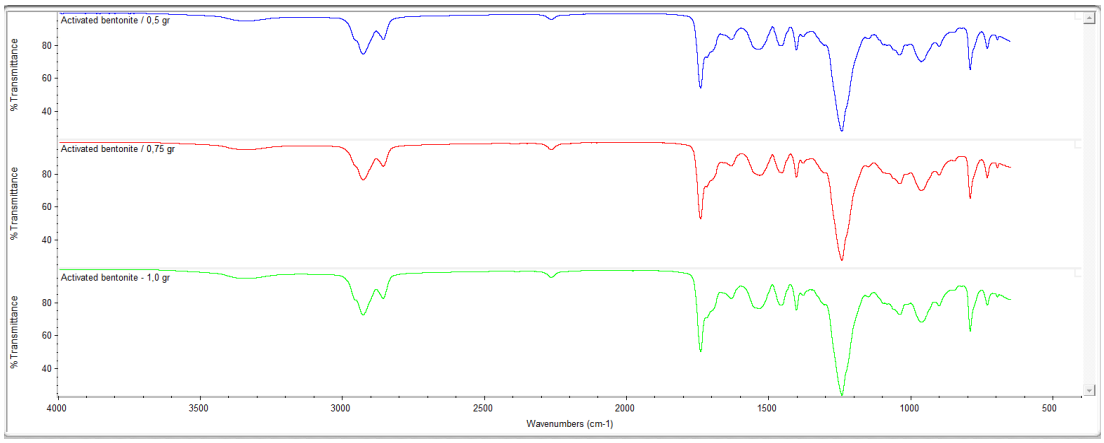


**Figure A.4 :** FTIR analysis of activated bentonite/PU NC in common scale.

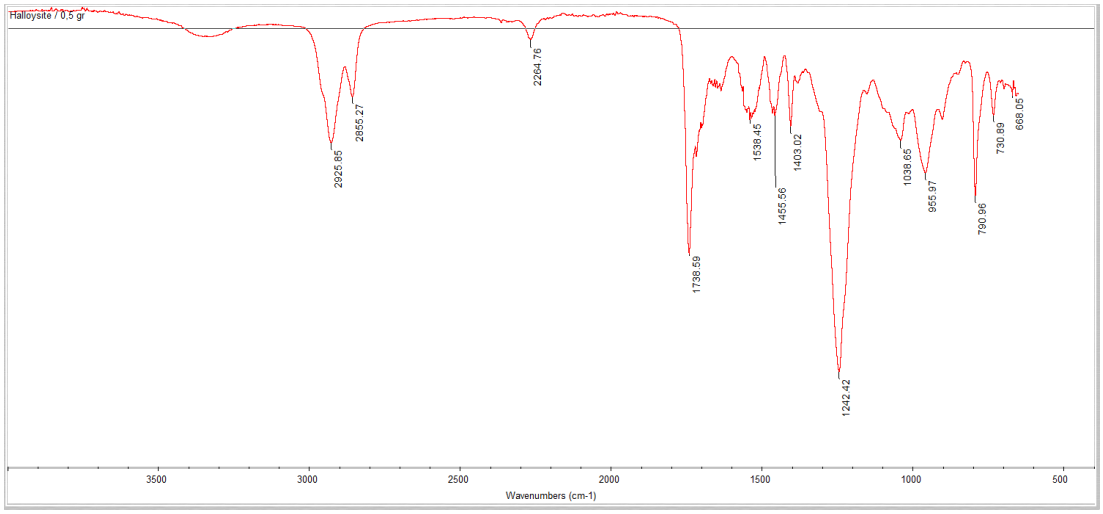


**Figure A.5 :** FTIR analysis of 3.6% halloysite/PU NC.

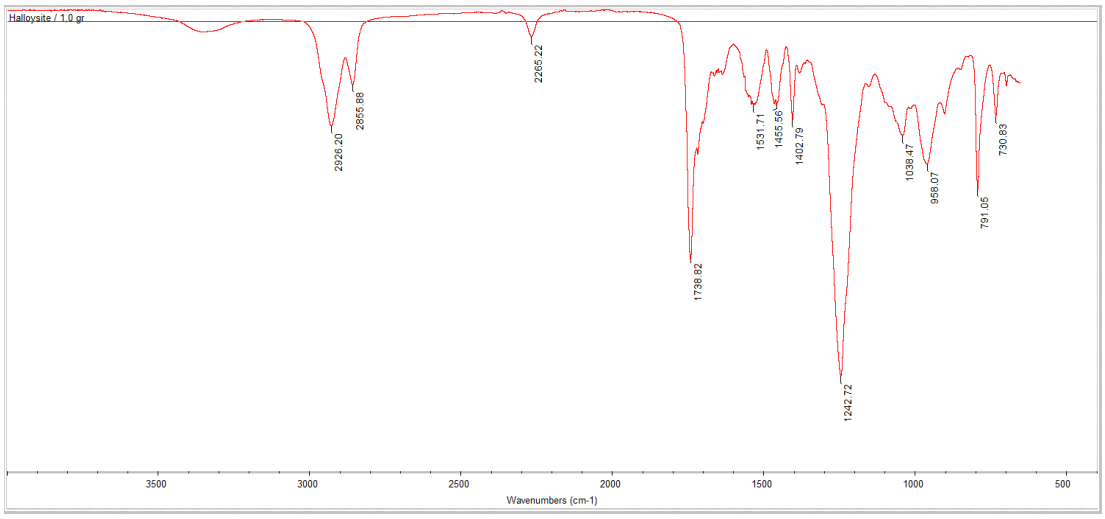


**Figure A.6 :** FTIR analysis of 7.0% halloysite/PU NC.

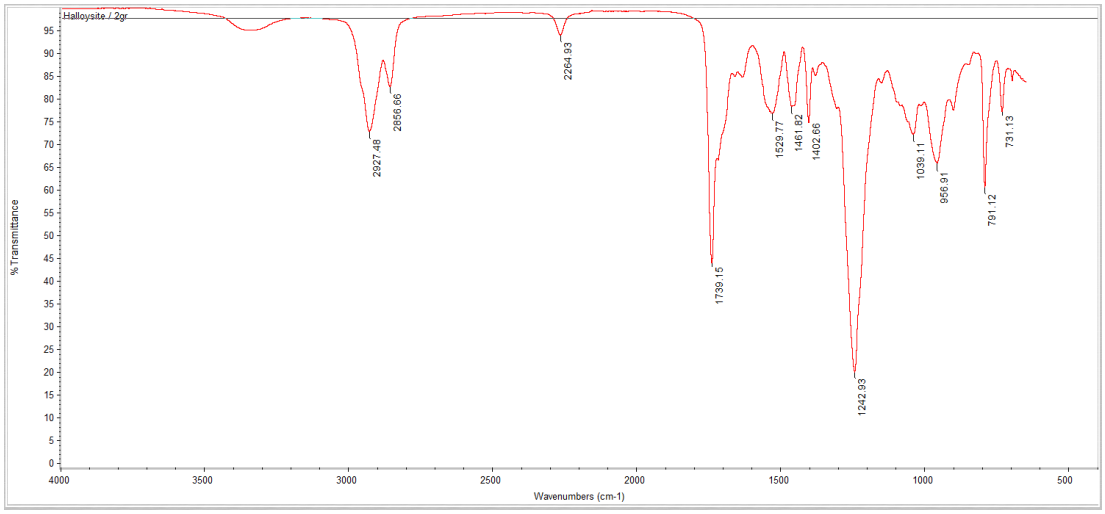


**Figure A.7 :** FTIR analysis of 13% halloysite/PU NC.

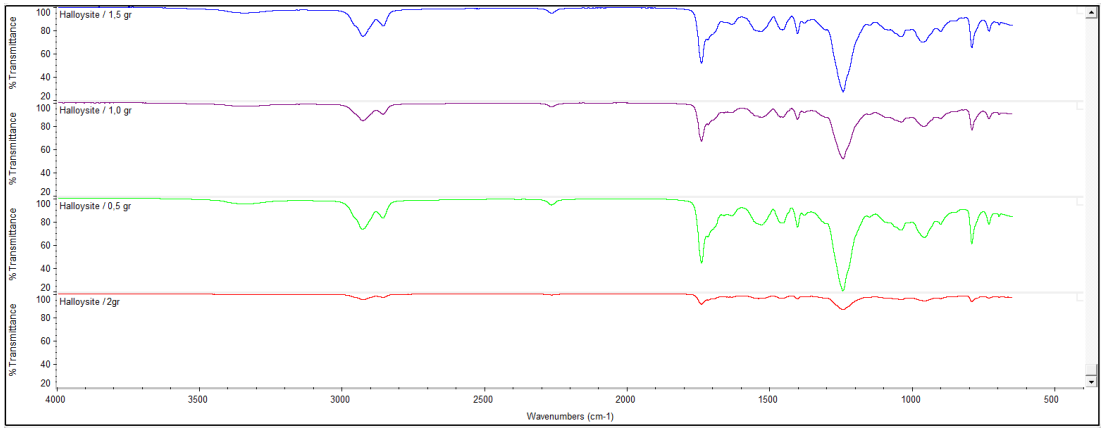


**Figure A.8 :** FTIR analysis of halloysite/PU NC in common scale.

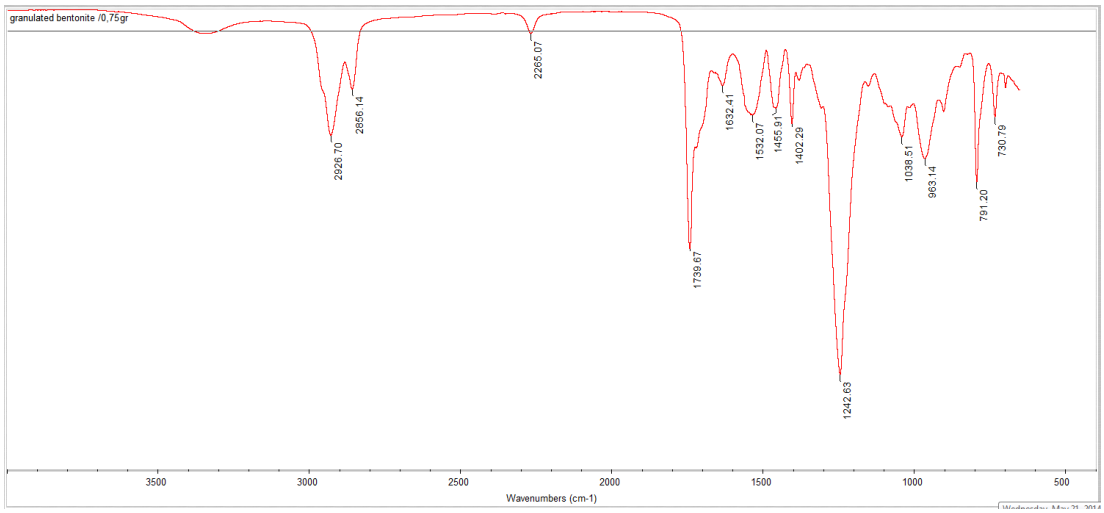


**Figure A.9 :** FTIR analysis of 5.3% raw bentonite/PU NC.

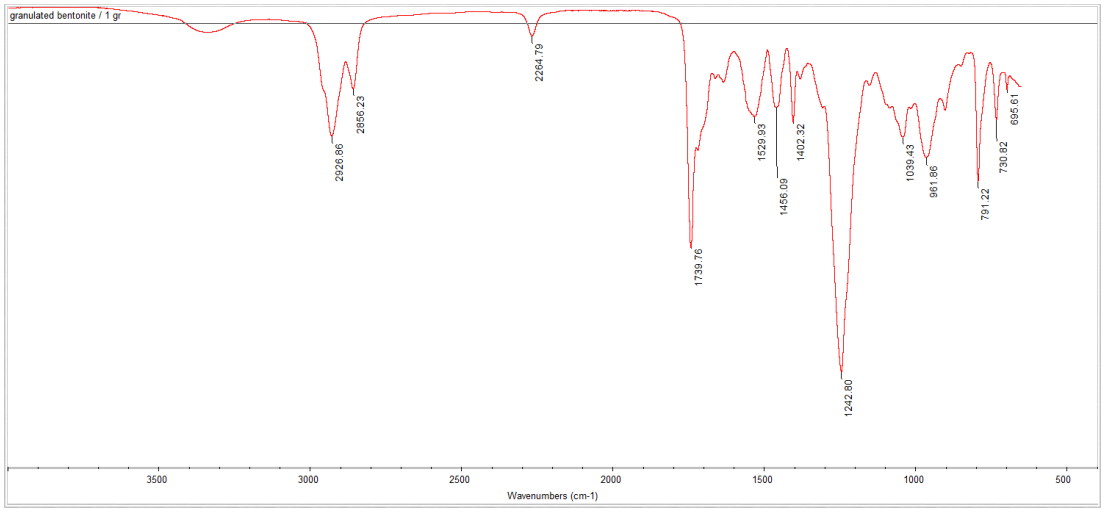


**Figure A.10 :** FTIR analysis of 7.0% raw bentonite/PU NC.

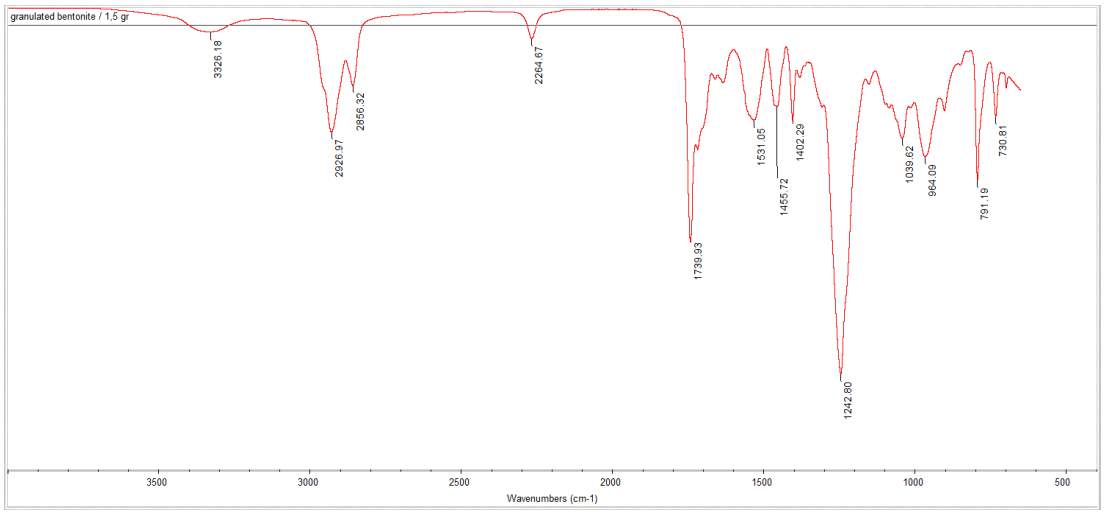


**Figure A.11 :** FTIR analysis of 10% raw bentonite/PU NC.

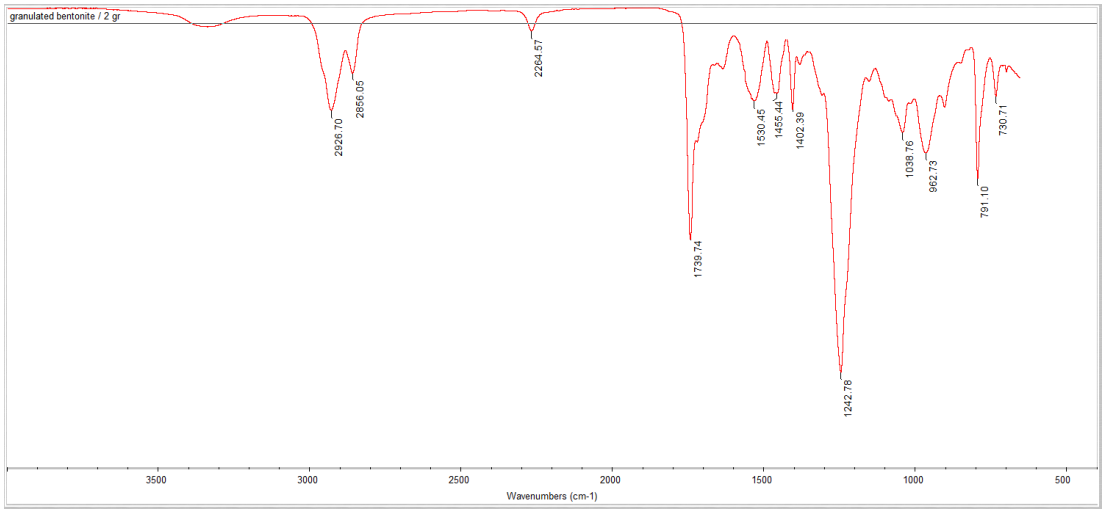


**Figure A.12 :** FTIR analysis of 13% raw bentonite/PU NC.

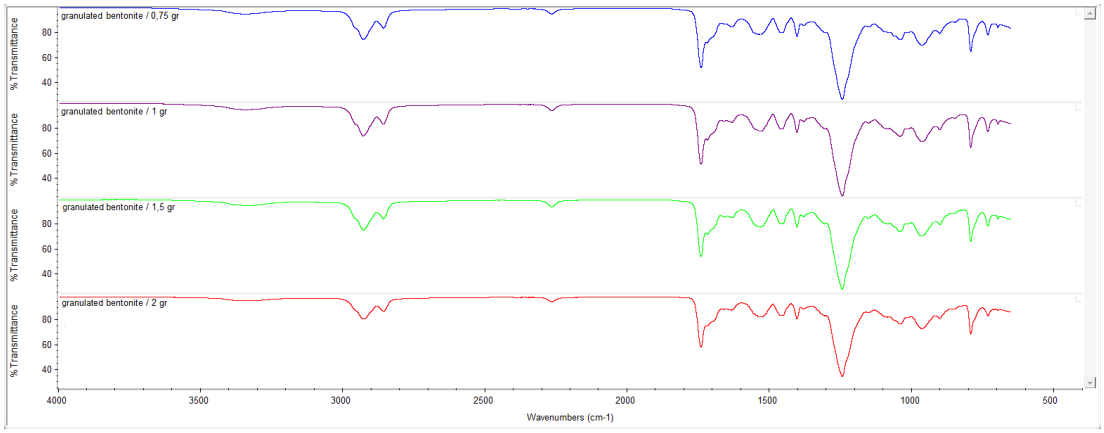


**Figure A.13 :** FTIR analysis of raw bentonite/PU NC in common scale.

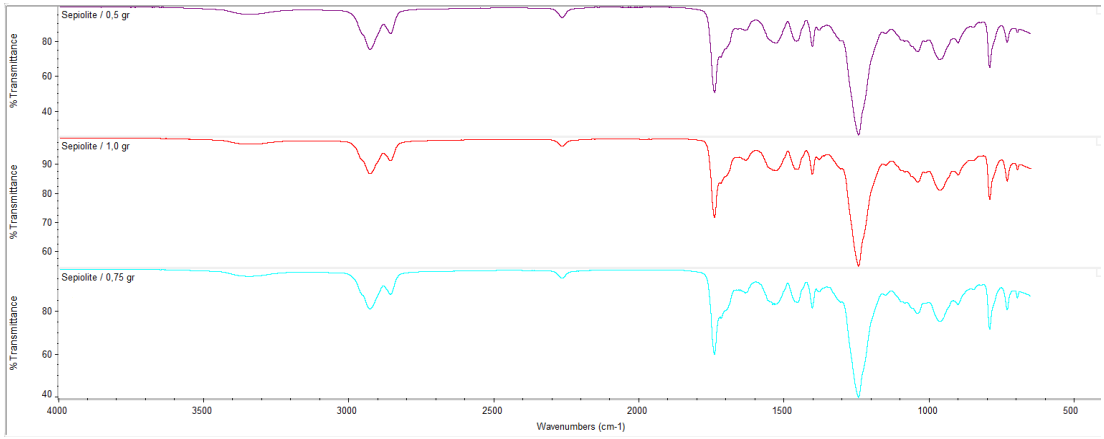


**Figure A.14 :** FTIR analysis of 3.6% sepiolite/PU NC.

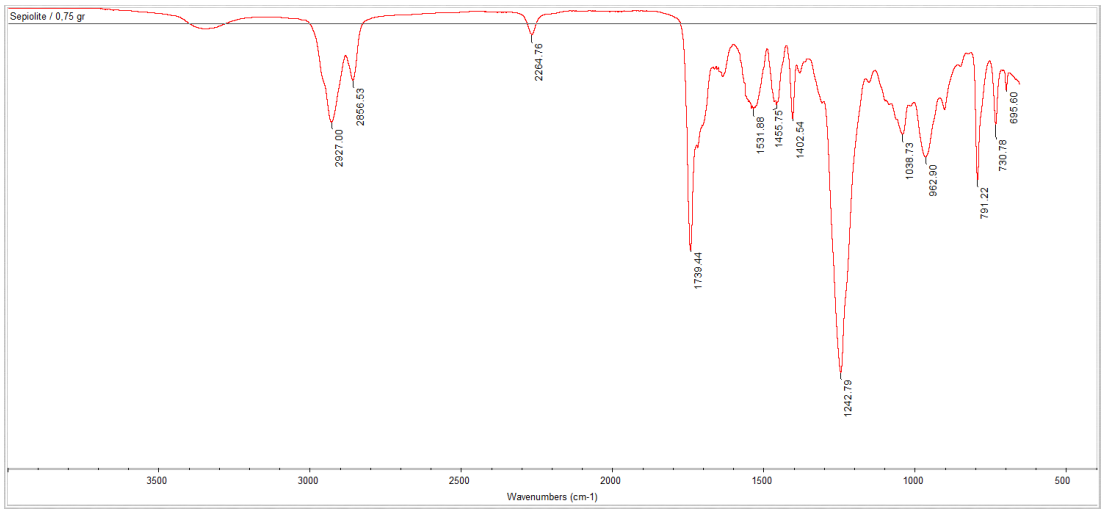


**Figure A.15 :** FTIR analysis of 5.3% sepiolite/PU NC.

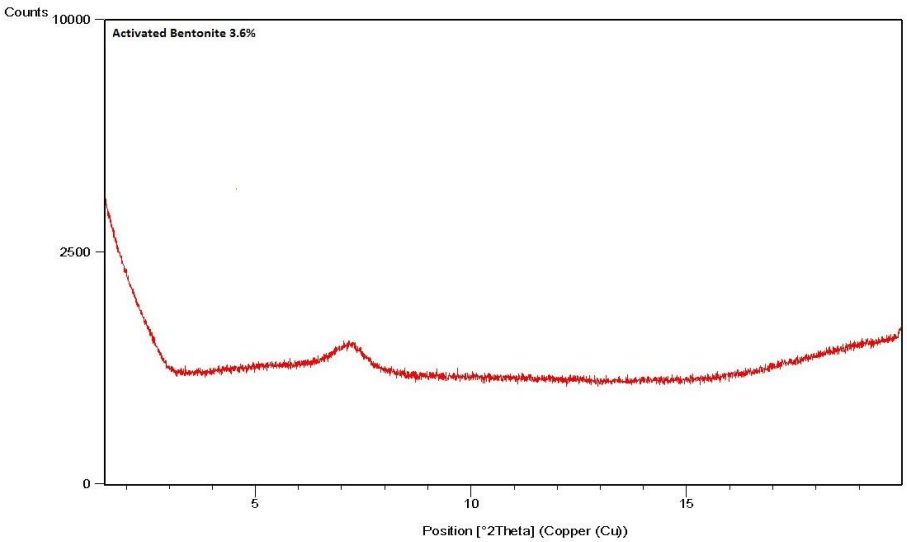


**Figure A.16 :** XRD analysis of 3.6% activated bentonite/PU NC.

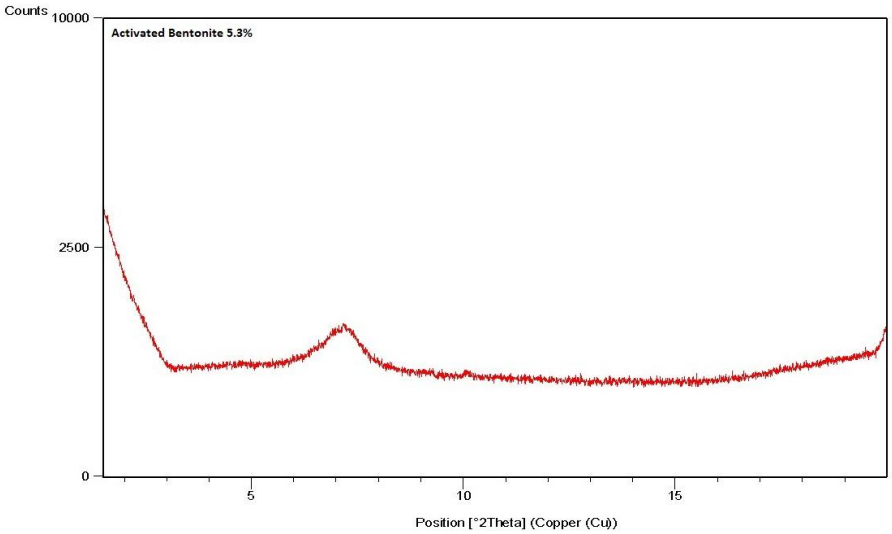


**Figure A.17 :** XRD analysis of 5.3% activated bentonite/PU NC.

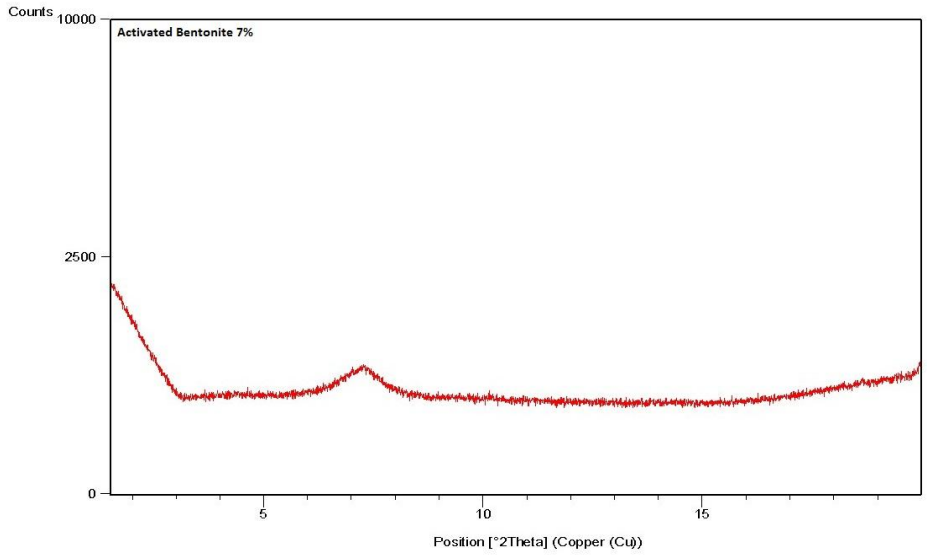


**Figure A.18 :** XRD analysis of 7.0% activated bentonite/PU NC.

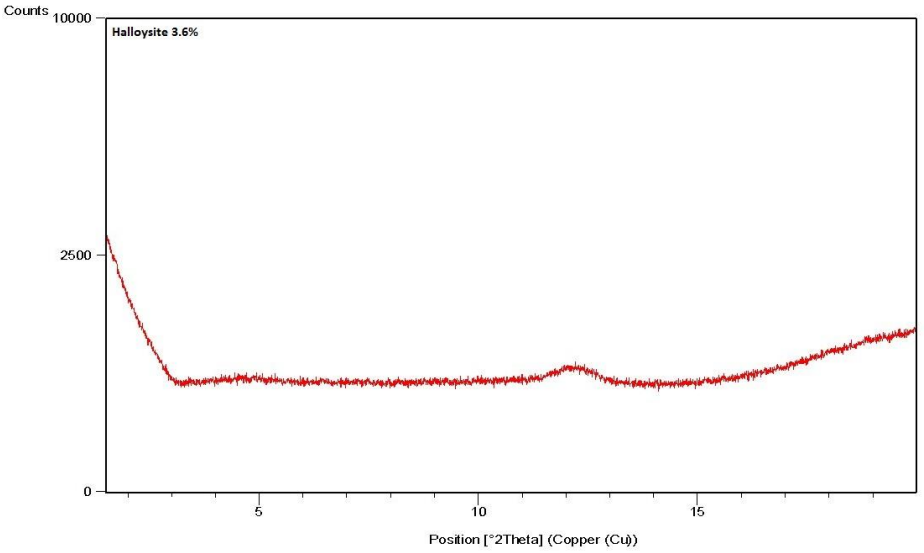


**Figure A.19 :** XRD analysis of 3.6% halloysite/PU NC.

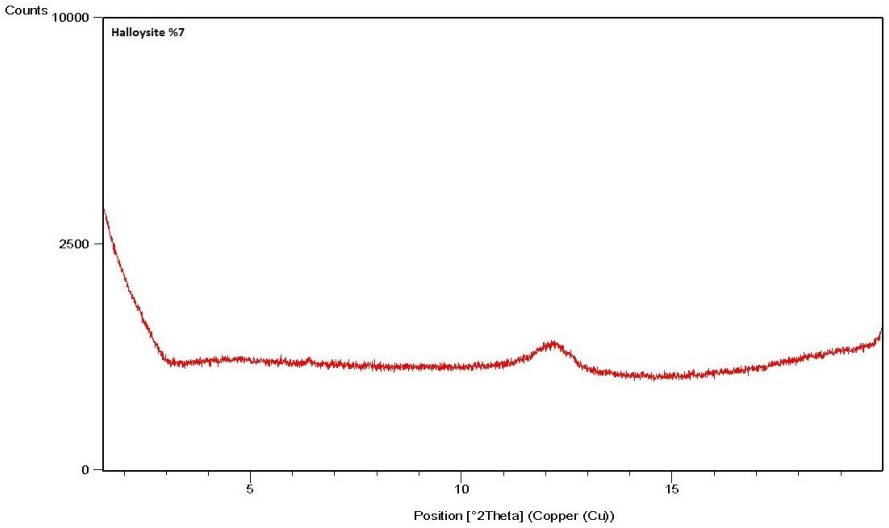


**Figure A.20 :** XRD analysis of 7.0% halloysite/PU NC.

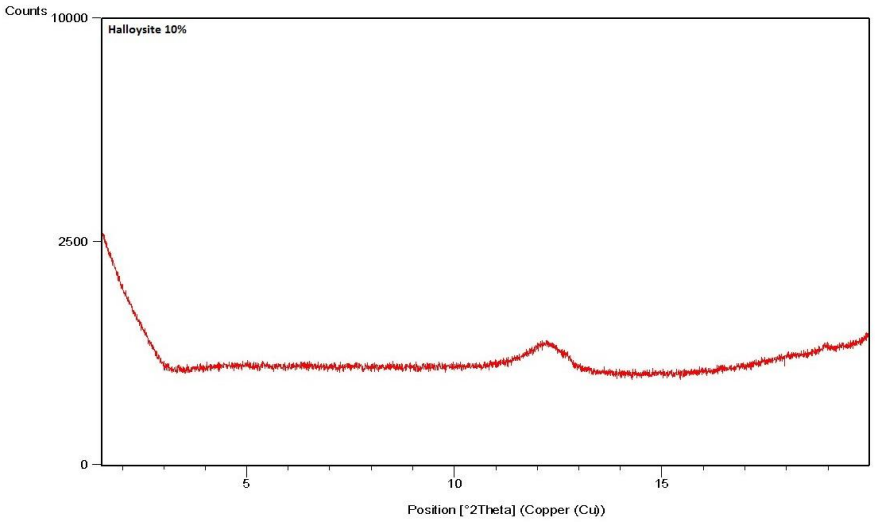


**Figure A.21 :** XRD analysis of 10% halloysite/PU NC.

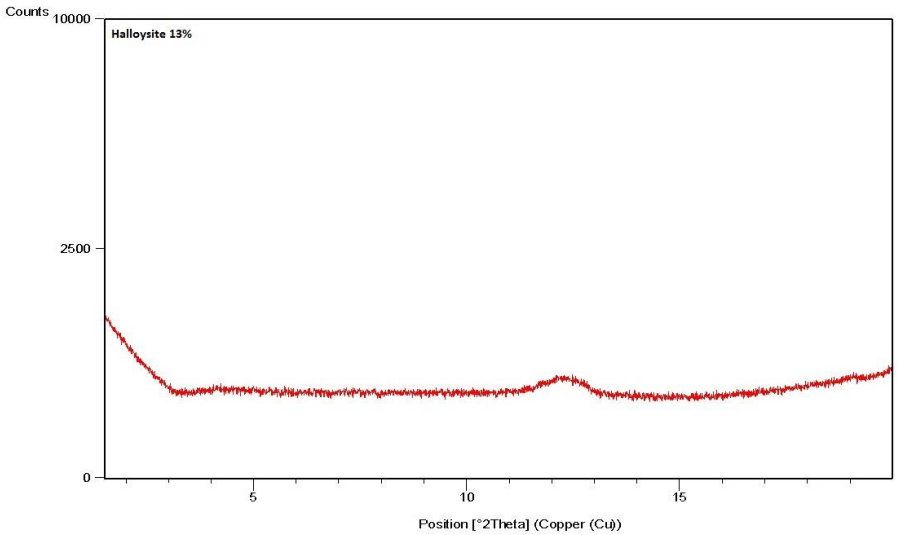


**Figure A.22 :** XRD analysis of 13% halloysite/PU NC.

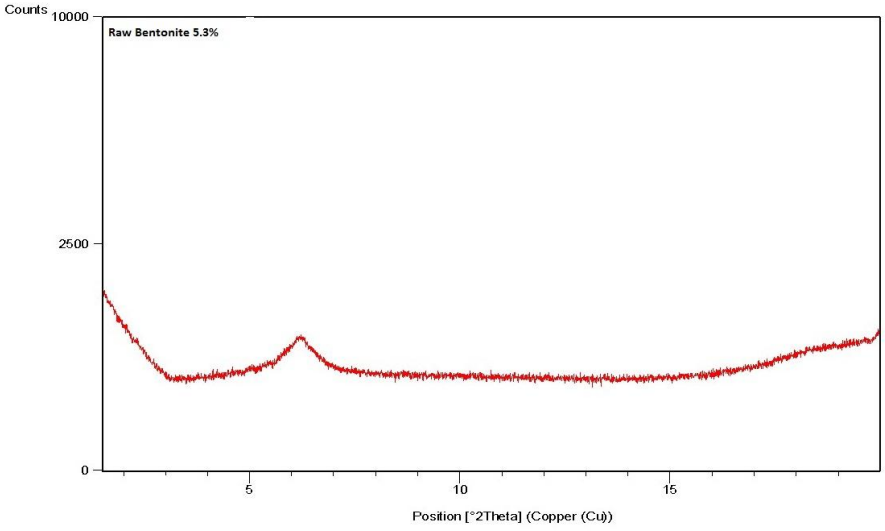


**Figure A.23 :** XRD analysis of 5.3% raw bentonite/PU NC.

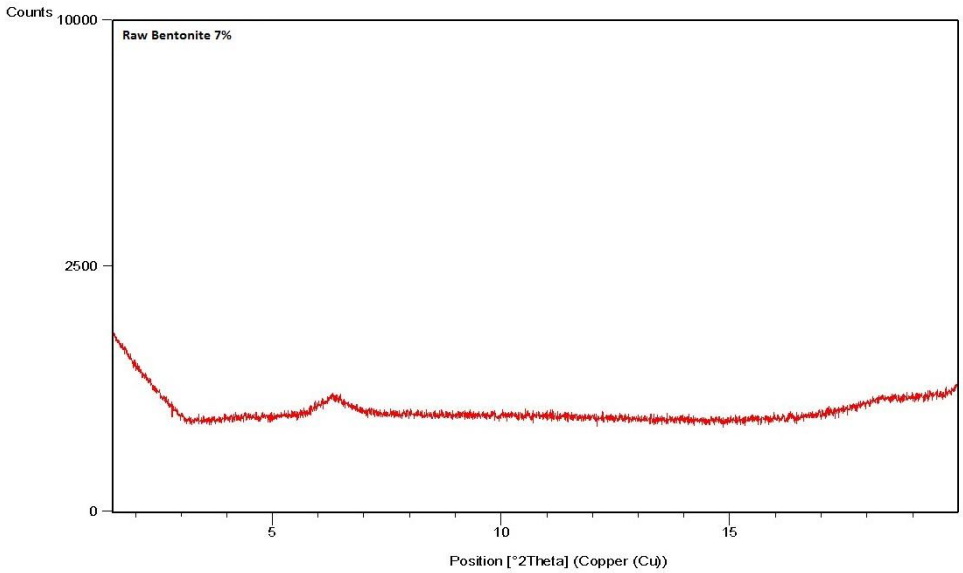


**Figure A.24 :** XRD analysis of 7.0% raw bentonite/PU NC.

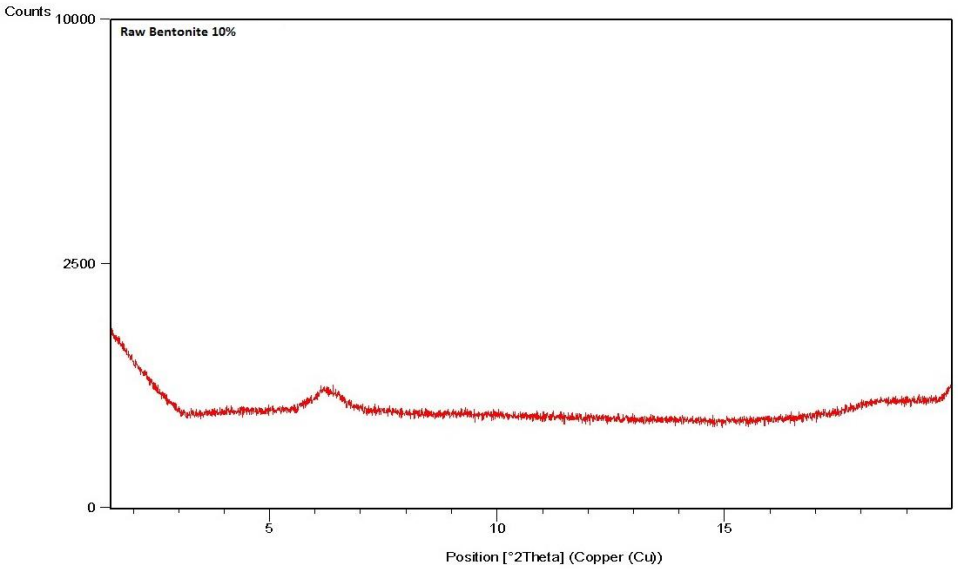


**Figure A.25 :** XRD analysis of 10% raw bentonite/PU NC.

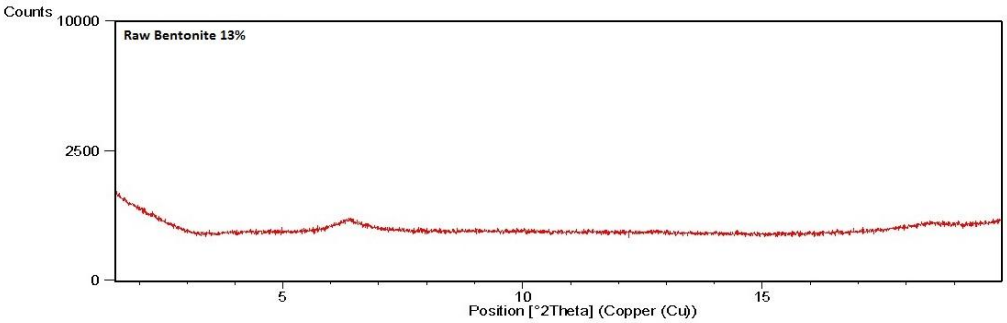


**Figure A.26 :** XRD analysis of 13% raw bentonite/PU NC.

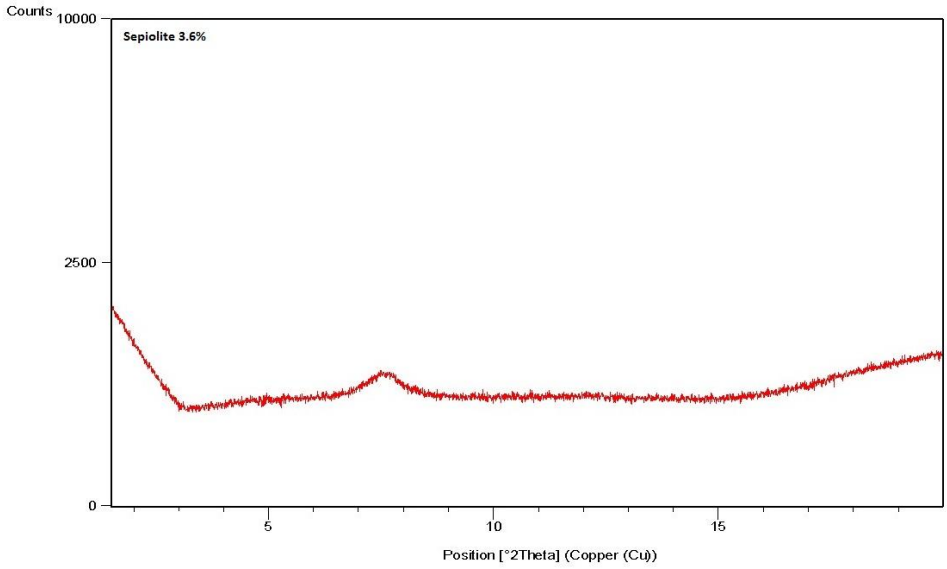


**Figure A.27 :** XRD analysis of 3.6% sepiolite/PU NC.

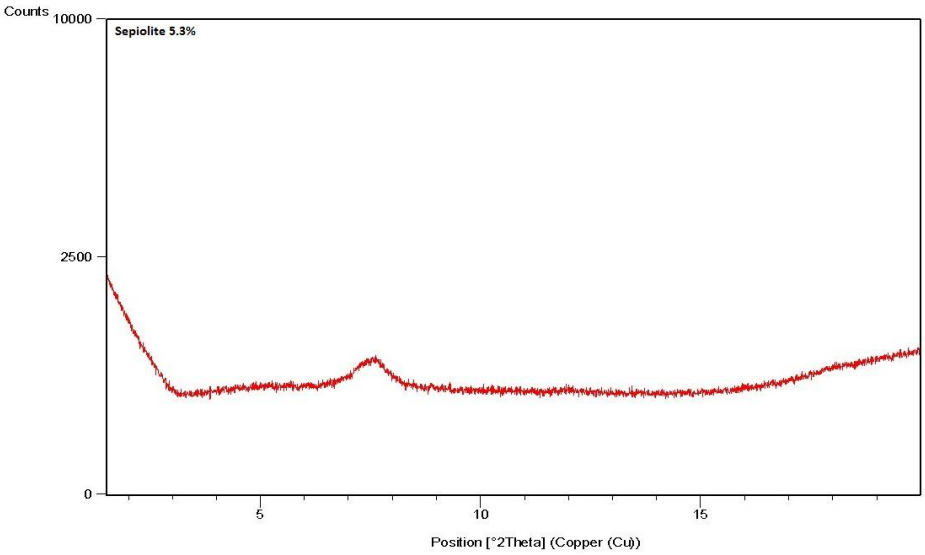


**Figure A.28 :** XRD analysis of 5.3% sepiolite/PU NC.

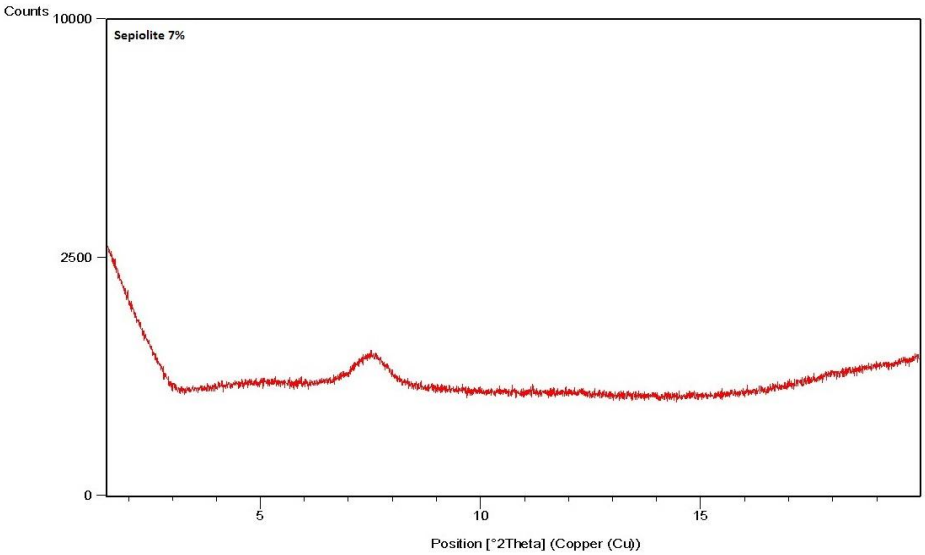


**Figure A.29 :** XRD analysis of 7.0% sepiolite/PU NC.

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